UNIVERSITÉ DU QUÉBEC À MONTRÉAL

# RECYCLING THERMOSET COMPOSITE WASTE FROM THE AEROSPACE INDUSTRY

THESIS

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# RECYCLAGE DE DÉCHETS COMPOSITES THERMODURCISSABLES DE L'INDUSTRIE AÉRONAUTIQUE

MÉMOIRE

PRÉSENTÉ

COMME EXIGENCE PARTIELLE

DE LA MAÎTRISE EN CHIMIE

PAR

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# RÉSUMÉ

L'utilisation croissante des composites thermodurcissables renforcés de fibres de carbone (CFRPs), dans l'industrie aérospatiale, génère une quantité importante de déchets composites. Actuellement, la grande majorité de ces déchets composites sont envoyés dans les sites d'enfouissements. Donc, le recyclage des CFRPs permettrait de réduire la quantité de déchets composites et de récupérer des fibres de carbone.

Dans ce travail, les fibres de carbone recyclées "Prepreg" et "Tooling" ont été récupérées des CFRPs générés par l'industrie aéronautique canadienne avec un procédé de pyrolyse, à l'échelle commerciale, de Materials Innovation Technologies.

Les propriétés morphologiques, mécaniques et de surface des fibres de carbone recyclées ont été caractérisées par les techniques suivantes; microscopie électronique à balayage (MEB), mesures de densité par pycnométrie, tests de micro-traction, analyse BET, spectroscopie de photoélectrons rayons-x (XPS), analyse de mouillabilité par l'angle de contact dynamique et l'adhérence interfaciale par des essais de micro-gouttelettes avec une résine époxy. Les fibres de carbone recyclées conservent une bonne tenue mécanique et adhésive, de qualité comparable à des fibres de carbone neuves. Cependant, le traitement par pyrolyse a modifié leurs propriétés de surface par l'élimination de la résine et de la couche de "Sizing", révélant ainsi les topographies de surface.

Le chapitre I couvre la théorie sur les matériaux composites structuraux, les systèmes de résine et les fibres de carbone. De plus, des technologies de recyclage des CFRPs sont présentées et évaluées. La pyrolyse a été déterminée comme la technologie la plus économiquement viable, car elle permet de récupérer des fibres de carbone de hautes qualités. Enfin, plusieurs méthodes de re-fabrication des composites thermodurcissables utilisant les fibres de carbone recyclées ont été explorées.

Le chapitre II présente les résultats de l'effet du traitement par pyrolyse sur la mouillabilité et l'adhérence interfaciale des fibres de carbone recyclées avec une résine époxy. La mouillabilité et l'adhérence entre la surface des fibres de carbone recyclées et la résine époxy sont principalement affectées par les interactions acide / base de Lewis des groupes fonctionnels oxygénés de surface, ainsi que, par l'encastrement ("Interlock") mécanique. L'encastrement mécanique semble être le paramètre prédominant, car les fibres striés de "Prepreg" ont une adhésion interfaciale, avec une résine époxy, plus élevée que les fibres lisses de "Tooling". Par conséquent, les topographies ont été jugées extrêmement

importantes pour prédire la performance des composites re-fabriqués avec des fibres de carbone recyclées.

Le chapitre III présente une méthode de re-fabrication des composites thermoducissables contenant des fibres de carbone recyclées. Les fibres de carbone recyclées ont été réintegrées dans de nouveaux composites thermodurcissables en fabriquant des plaques résine époxy / fibres de carbone recyclées. Un procédé de cardage suivi d'un traitement par ultrasons permet de fabriquer des mattes de fibre de carbone recyclées, qui sont alignées de façon aléatoire. Ces mattes ont été utilisées pour fabriquer des plaques résine époxy / fibres de carbone recyclées, avec des fractions volumétrique de fibre jusqu' à 40 %, par le moulage infusion / compression.

Les propriétés mécaniques des plaques composites ont été évaluées par des essais de traction et flexion. Les plaques composites qui contiennent des fibres de carbone recyclées ont des propriétés mécaniques comparables à celles qui contiennent des fibres de carbone neuves. Ce travail démontre l'énorme potentiel de re-fabrication des composites thermodurcissables à partir fibres de carbone recyclées. Ces matériaux peuvent être utilisés dans des applications adaptées à l'industrie aérospatiale ou dans d'autres marchés.

# ABSTRACT

The increasing use of carbon fiber reinforced thermoset composites in the aerospace industry has generated a significant amount of manufacturing and end of life waste. Currently, the vast majority of this waste is sent to landfills, as such the reycling of carbon fiber reinforced thermoset composite waste aims to reduce its disposal in landfills, and to recover the potentially valuable recycled carbon fibers.

In this work, chopped recycled carbon fibers from prepreg and tooling were recovered from carbon fiber reinforced thermoset composite waste generated by the Canadian aircraft industry, using Materials Innovation Technologies commercial scale pyrolysis process. The morphological, mechanical and surface properties of the recycled carbon fibers were characterized by scanning electron microscopy (SEM), density measurements by pycnometry, micro-tensile testing, BET analysis, x-ray photoelectron spectroscopy (XPS), wettability analysis by dynamic contact angle measurement and interfacial adhesion with epoxy resin by micro-droplet testing. The recycled carbon fibers appeared relatively undamaged, exhibiting a comparable mechanical and adhesive performance to virgin carbon fibers. However, pyrolysis processing altered their surface properties by effectively removing resin and sizing, thereby revealing surface topographies.

In Chapter I, a background is provided examining composite structural materials, resin systems, and carbon fibers. In addition, recycling technologies for carbon fiber reinforced thermoset composite waste are identified and evaluated. Fiber reclamation was determined to be the most economically viable technology, as it can recover potentially valuable recycled carbon fibers. Finally, several methods for re-manufacturing thermoset composites using recycled carbon fibers were explored.

In Chapter II, the effect of pyrolysis processing on the wettability and interfacial adhesion of recycled carbon fibers with epoxy resin is evaluated. Wetting and interfacial adhesion between the surface of the recycled carbon fibers and epoxy resin were found to be predominantly affected by Lewis acid / base interactions of oxygenated surface functional groups, as well as, by mechanical interlocking. Mechanical interlocking appeared to be the more important parameter, as the striated prepreg fibers out-performed the smooth tooling fibers in interfacial adhesion with epoxy resin. Therefore, surface topographies were found to be extremely important when predicting the performance of re-manufactured composites containing recycled carbon fibers.

In Chapter III, the recycled carbon fibers were re-manufactured into new thermoset composites by reintegrating them as chopped fiber reinforcement in epoxy plates. A carding process followed by an ultrasound treatment produced randomly aligned recycled carbon fiber mats. These mats were used to fabricate epoxy / recycled carbon fiber plates, with fiber volume fractions up to 40 vol. %, by infusion / compression molding. The mechanical properties of the composite plates were evaluated by tensile and flexural testing, and were found to be comparable to an equivalent containing virgin carbon fibers.

This thesis confirms the huge potential of re-manufacturing thermoset composites from recycled carbon fibers, as they exhibited similar performance to virgin carbon fibers. Such materials might be suitable applications in the aerospace industry or in other markets.

# CHAPITRE I

# INTRODUCTION

## 1.1 Context

The difficult issue of recycling thermoset structural composites has been the subject of much investigation over the last 15 years, and on a large scale, is still an unsolved problem. Thermoset structural composites have been used in aircraft components for many years, as they significantly reduce aircraft weight and fuel consumption. Currently, composite waste coming from the aerospace industry is either ground up into fillers, incinerated, or digested using environmentally questionable technologies; however, the vast majority of composite waste in North America is sent to landfills. Aircraft manufacturers are thus under serious pressure to reduce waste through recycling or reuse, affecting both in-process waste and end-of-life disposal. It is therefore important to continue research on the thermoset structural composite recycling in order to become more environmentally friendly.

## 1.2 Mechanical Properties of Materials

Structural materials are subject to external loading during use. Therefore, understanding how a material deforms or breaks is critical in ensuring a stable structure. The relationship between stress and strain reveals many important mechanical properties as depicted graphically in Figure 1.1 [1, 2].

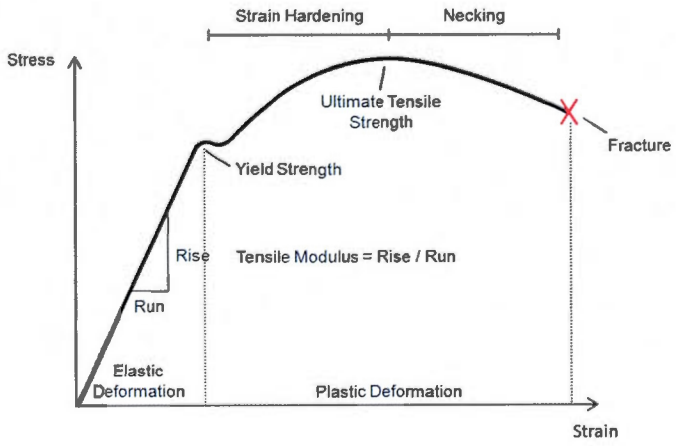



**Figure 1.1** Idealised Stress-Strain behavior of a ductile material under tension [2].

In order to compare specimens of different sizes, external loads are calculated per unit area. Force divided by area is called stress, and is measured in pressure units (Pa). In tension and compression, the area is perpendicular to the external load, while in shear or torsion, the area is perpendicular to the axis of rotation. Stress is calculated by:

$$\sigma \text{ or } \tau = \frac{F}{A_0} \tag{1.1}$$

Where $\sigma$ (Pa) is the tensile or compressive stress, $\tau$ (Pa) is the shear stress, $F$ (N) is force and $A_0$ ($m^2$) is the area.

Under tension and compression, the material deforms and elongates. In order to compare specimens of different lengths, strain is measured as a change in length divided by the specimen's original length. Strain is calculated by:

$$\varepsilon = \frac{\Delta L}{L_0} \tag{1.2}$$

Where $\varepsilon$ is the strain, $\Delta L$ (m) is the change in length, and $L_0$ (m) is the original length. Strain is often expressed as a percentage.

Materials can undergo two types of deformation, either elastic or plastic. Elastic deformation is reversible and non-permanent, while plastic deformation is irreversible and permanent. In tensile testing (Figure 1.1), when the deformation is elastic, the slope of the stress-strain curve follows Hooke's law, defined as:

$$\sigma = E\varepsilon \tag{1.3}$$

Where $E$ is Young's modulus also known as the modulus of elasticity.

The following properties can be also be obtained by the relationship between stress and strain of a material under tension (Figure 1.1):

**Tensile Strength:** The tensile strength is also known as the ultimate strength, and corresponds to the maximum tensile stress a material can withstand under tension. Tensile strength is generally expressed in units of MPa = $10^6$ Pa

**Yield point:** If the stress is too large, Hooke's law no longer applies, as stress is no longer proportional to strain. This is called the yield point, and it occurs when the material begins to deform plastically.

**Yield strength:** The Yield strength corresponds to the stress at the yield point. Structural materials are designed to undergo only elastic deformation during use. Therefore, in many cases, the yield strength is a more important parameter than the tensile strength.

**Tensile Modulus:** The tensile modulus measures the stiffness of a material. It is defined as the slope in the elastic region of the stress-strain curve, and corresponds to Young's modulus. Tensile modulus is generally expressed in units of GPa = $10^9$ Pa

**Toughness:** Toughness is the ability of a material to deform plastically without fracturing. It corresponds to the area under the plastic region of the stress-strain curve.

**Resilience:** Resilience is the capacity of a material to deform elastically. It corresponds to the area under the elastic region of the stress-strain curve.

**Ductility:** Ductility is the ability of a material to deform without fracturing. It corresponds to the maximum strain before fracturing (maximum elongation). It is the opposite of brittleness.

The behavior of materials can be broadly classified into two categories; brittle and ductile, as shown in Figure 1.2 [3, 4]. Ductile materials exhibit large strains before fracturing, while brittle materials fracture at much lower strains. The yield region for ductile materials takes up the majority of the stress-strain curve, whereas for brittle materials, it is nearly non-existent. Additionally, brittle materials have relatively high tensile moduli and strengths compared to ductile materials.

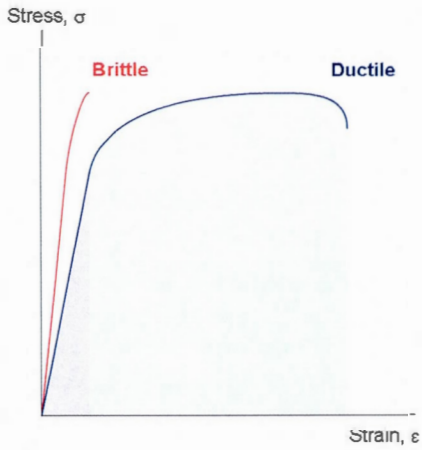



**Figure 1.2** Typical stress-strain behavior for brittle and ductile materials [3, 4].

## 1.3 Composite Structural Materials

Composite structural materials consist of a matrix, usually a polymer based resin system, which encapsulates reinforcing fibers [5, 6]. The purpose of the matrix is to bind reinforcing fibers together, and to transfer external loads onto them, producing a structurally sound material. Additionally, fillers and additives may be added for various purposes. Common reinforcing fibers include carbon, glass, and aramid fibers; while, resin systems include both thermoplastic and thermosetting resins. As shown in Figure 1.3, reinforcing fibers have exceptional strength and stiffness, and undergo elastic deformation (brittle) under external load; while resin systems have poor strength and stiffness, and undergo plastic

deformation (ductile). Thus, the properties of composite structural materials depend on both reinforcing fibers and resin matrix, and are determined by [5, 6]:

1. The mechanical properties of the reinforcing fibers.
2. The mechanical properties of the resin matrix.
3. The volumetric ratio between reinforcing fibers and resin matrix.
4. The geometry and orientation of the reinforcing fibers.
5. The interfacial adhesion between reinforcing fibers and resin matrix.

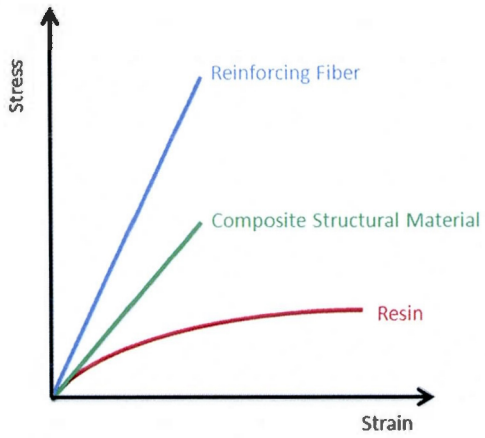



**Figure 1.3** Typical stress - strain relationship for composite materials, and their components, undergoing tensile testing [6].

As shown in Figure 1.4, there are four main external loads that composite structural materials need to withstand; tension, compression, shearing and flexion. The response of structural composite materials to tensile loading depends on the strength and stiffness of the reinforcing fibers. On the other hand, their response to compressive loading depends on the stiffness and adhesive properties of the resin matrix; and to shear loading, on the ability of the resin matrix to transfer stresses across the material. Finally, flexural loading is a combination of tension, compression, and shearing.

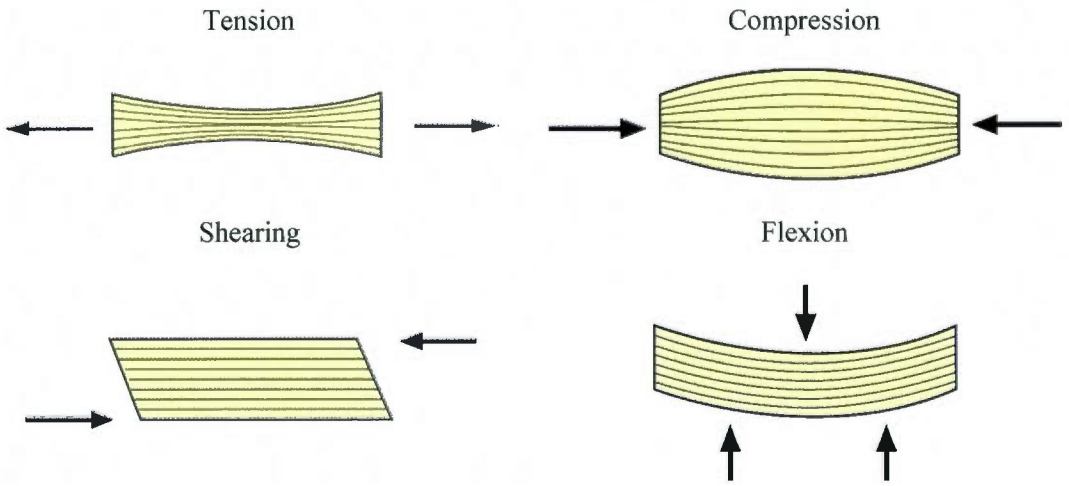



**Figure 1.4** External loading on composite structural materials [6].

Composites structural materials have been used in aircraft design for many years, as they significantly reduce aircraft weight and fuel consumption. Carbon fiber reinforced thermoset composites, also known as carbon fiber reinforced plastics (CFRPs), the main focus of this thesis, are characterized by their excellent mechanical properties, as well as low densities compared to traditional structural materials, as shown in Figure 1.5-1.7.

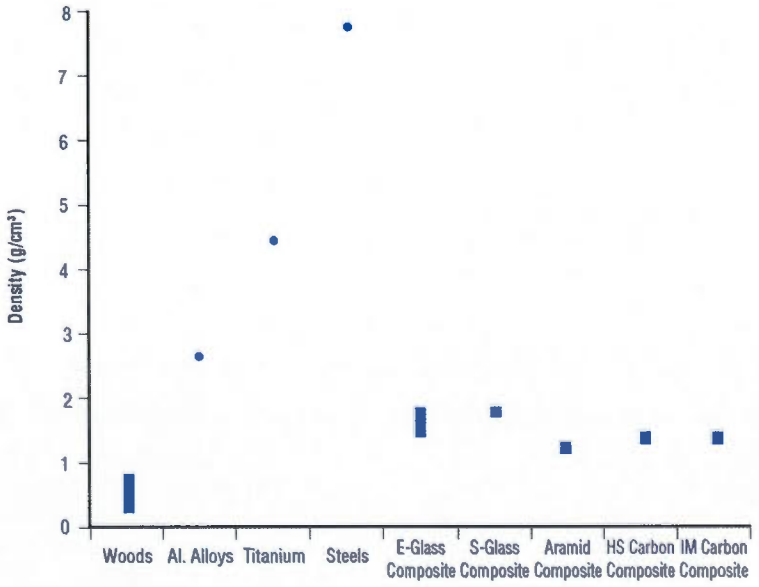



**Figure 1.5** Density (g / $cm^3$) of common structural materials [6].

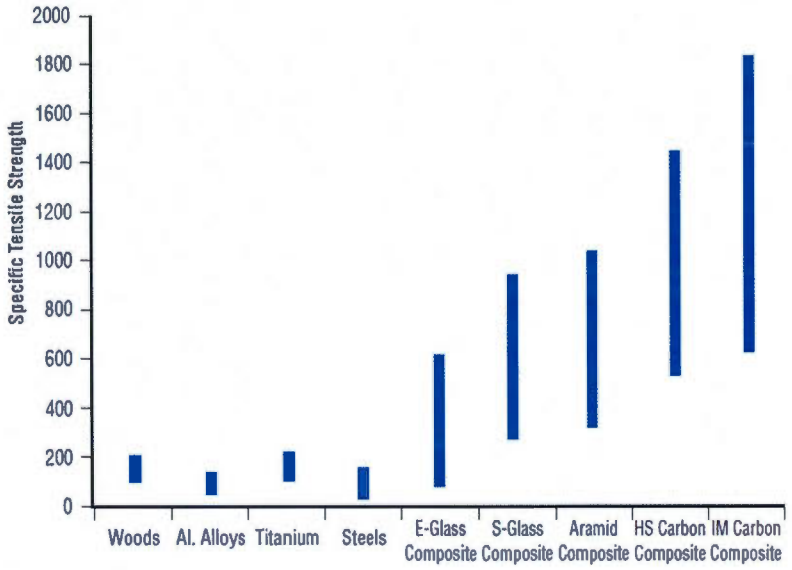



**Figure 1.6** Specific tensile strength (MPa $cm^3$ / g) of common structural materials [6].

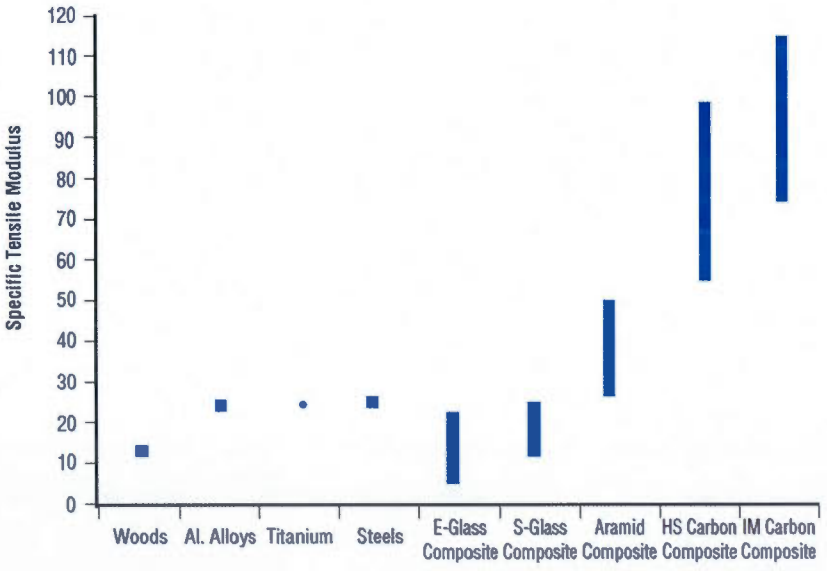



**Figure 1.7** Specific tensile modulus (GPa $cm^3$ / g) of common structural materials [6].

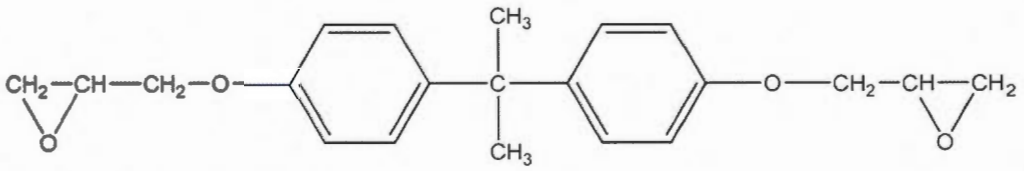
Finally, structural composite materials can be produced through filament winding, tape winding, pultrusion, compression molding, vacuum bagging, liquid molding and injection molding of fiber pre-forms with resin systems [5, 6].

## 1.4 Resin Systems

Resin Systems utilized in structural composites require adequate mechanical, adhesive and toughness properties, as well as, resistance to environmental degradation. The two main types of resin systems are thermoplastics and thermosets [5-7]. When heated, thermoplastics soften and eventually melt, hardening again with cooling. In theory, melting and hardening can be repeated as often as desired without any adverse effects on material properties. Examples of thermoplastics include; polyethylene (PE), polypropylene (PP), polyamide (PA), polyethylene terephthalate (PET), polyphenylene sulfide (PPS), polyether ether ketone (PEEK) and polyether imide (PEI). Thermosets are different from thermoplastics, as they require curing, causing the polymer chains to cross-link and harden. Curing occurs when resin and hardener, or resin and catalyst, are mixed together and undergo a non-reversible chemical reaction. Once cured, thermosets will not melt if heated again, although above the glass transition temperature ($T_g$), the mechanical properties will change significantly, as the molecular structure changes from that of a rigid crystalline polymer to a more flexible, amorphous polymer. This causes the stiffness of the resin to drop sharply. The most common thermosets includes unsaturated polyesters, epoxies, vinyl esters and phenolic resins.

Epoxies are by far the most widely used resin system, constituting over 90 % of all CFRPs [7]. Epoxies out-perform most other resin systems in terms of mechanical and adhesive properties, as well as, resistance to environmental degradation. They are extensively used in high performance applications such as aerospace, defence, and sporting goods. A typical epoxy molecule is presented in Figure 1.8a [6].

a.




b.


**Figure 1.8** a) Chemical Structure of a typical Epoxy (Diglycidyl Ether of Bisphenol-A), and b) Addition reaction of amine with epoxy groups [6].

Epoxy molecules are long chain structures with reactive epoxy groups at either end. In the specific case of Diglycidyl Ether of Bisphenol-A, the absence of ester groups (such as in vinyl esters) means that they are water resistant. The two ring groups of the Bisphenol-A moiety are capable of absorbing both mechanical and thermal stresses better than linear polymers. As shown in Figure 1.8b, when curing epoxy resin with an amine hardener, the epoxy and amine groups react by high yield addition reaction without any by-products. This form a complex three-dimensional structure as illustrated in Figure 1.9.

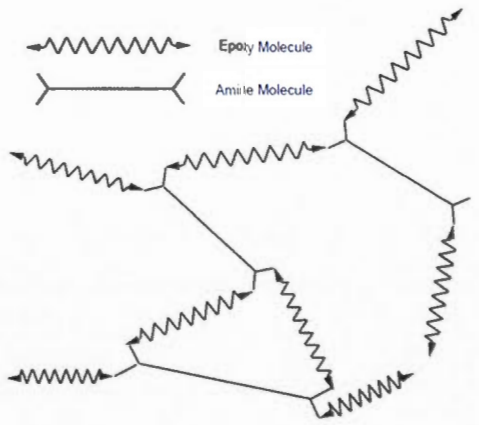



**Figure 1.9** Schematic representation of a cured epoxy resin system (3-D structure) [6].

## 1.5 Carbon Fibers

Carbon Fibers are used as reinforcing material in structural composites because they exhibit: high strength and stiffness, low density, and resistance to hostile environments [5, 6, 8-10]. The atomic structure of carbon fibers is similar to that of graphite (Figure 1.10). It consists of graphene sheets that are arranged in a hexagonal pattern. This forms basal planes that are aligned along the fiber axis, which interact with each other via weak Van der Waal bonding [8-10]. Carbon fibers require approximately 198-594 MJ / kg of manufacturing energy to produce [7].

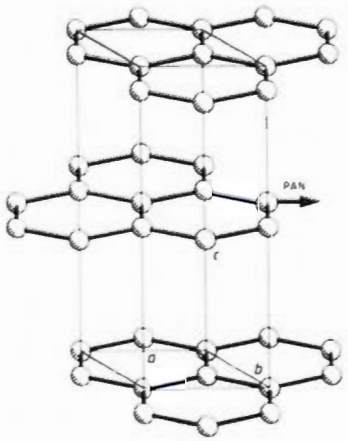



**Figure 1.10** Unit cell of Graphite [8].

Even though they are used interchangeably, there is a difference between carbon and graphite fibers [8-10]. The difference lies in the way the graphene sheets interlock. In graphitic fibers, the graphene sheets are stacked parallel to one another in a regular fashion, and contain upwards of 99 wt. % of carbon. In carbon fibers, the graphene sheets are randomly folded or crumpled together, and contain upwards of 92 wt. % of carbon. Graphitic fibers tend to have a much higher tensile modulus, while carbon fibers tend to have a much higher tensile strength. Graphitic fibers are more expensive because they require higher processing temperatures.

Carbon fibers are produced by 3 types of precursors: rayon, polyacrylonitrile (PAN), as well as, isotropic and liquid crystalline pitches [5, 6, 8-10]. This discussion will be limited to PAN based carbon fibers, as they are commonly used in the aerospace industry due to their high tensile strength. They consist of turbostratic graphite with basal planes aligned along the fiber axis. Turbostratic graphite corresponds to a highly oriented structure formed by parallel layers of condensed hexagonal rings having no three-dimensional order [8-10]. This forms a microstructure reminiscent of onion skin, and is depicted on Figure 1.11.

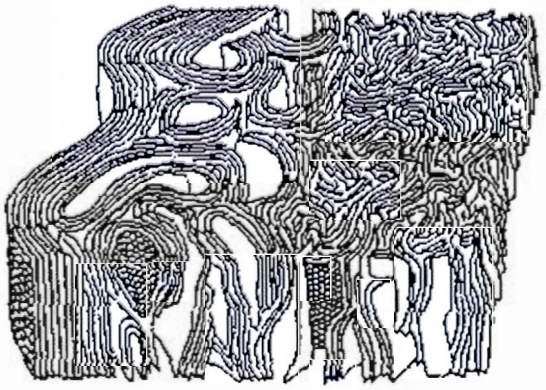


**Figure 1.11** Cross-section of PAN based Carbon Fibers [8-10].

PAN based carbon fibers are manufactured by controlled pyrolysis of stabilized PAN precursor fibers [5, 6, 8-10]. PAN precursor fibers are atactic, linear polymers containing highly polar nitrile pendant groups [9]. The transformation of PAN precursor fibers into carbon fibers consists of several steps: stabilization, carbonization, and surface treatment [9].

PAN precursor fibers are first stabilized by an oxidation process, at a temperature of about 200 to 400 °C in air [9], where the linear PAN molecules (thermoplastic) are converted into a cyclic structure (thermoset). Cross-linking of the polymer networks ensures that the fibers do not melt during processing. The next step is carbonization [9, 11], where the stabilized fibers are heated to temperatures ranging from 300°C to 1500°C in an inert atmosphere, in order to remove hydrogen, oxygen, nitrogen, and other non-carbon elements.

The carbonized fibers can be further graphitized at an even higher temperature up to around 3000 °C, to achieve even higher carbon content and higher tensile modulus, at the expense of tensile strength, in the fiber direction. The structure of PAN based carbon fibers at different points during carbonization and graphitization is shown on Figure 1.12 [11]. Finally, the relatively inert surface of carbon / graphite fibers undergo surface treatment [9, 11], to improve their adhesion to resin systems. The fibers may be etched using oxidizing agents such as chlorine, bromine, nitric acid or chlorates. Carbon fibers are also subjected to sizing. Sizing involves the addition of an epoxy coating, or other type of resin, onto their surface. This process allows thousands of fibers to stick together producing a single filament known as a tow. Furthermore, sizing prevents fiber abrasion and damage, improves handling, and provides an epoxy compatible surface. The tows are wound onto a spool, where they are stored until they are used during composite fabrication.

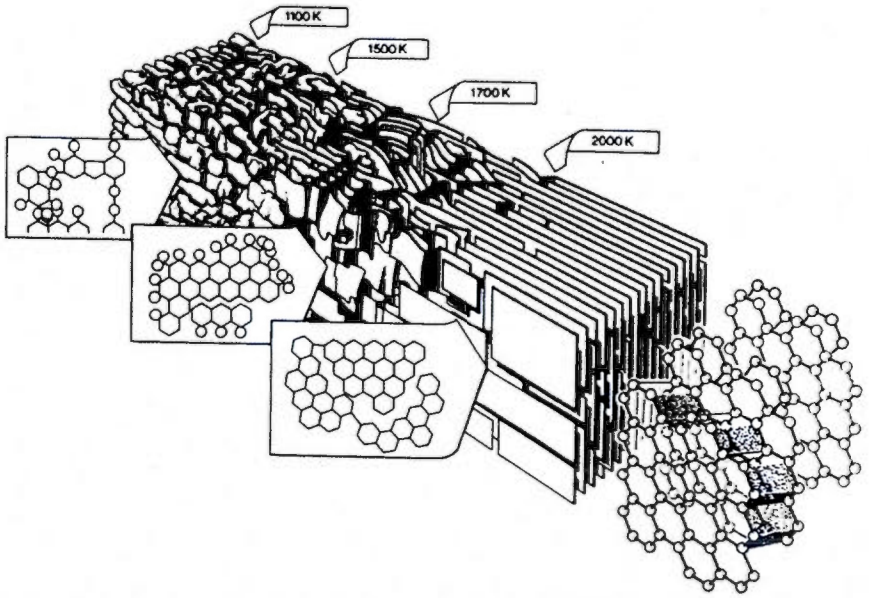



**Figure 1.12** Structure of a PAN based carbon fiber at different points during carbonization and graphitization [11].

The properties of carbon / graphite fibers are affected by many factors such as crystallinity, crystallite distribution, orientation of the graphene sheets, carbon content, and the amount of defects [9, 11]. Carbon fibers can be classified as: ultra high modulus (> 500

GPa), high modulus (> 300 GPa), intermediate modulus (> 200 GPa), low modulus (100 GPa), and high strength (> 4 GPa) carbon fibers.

As shown in Figure 1.13, PAN based carbon fibers break by the brittle-failure mechanism proposed by Reynolds and Sharp [8, 9]. The crystallites present in PAN based carbon fibers are not highly aligned, and misoriented crystallites are common. When a stress is applied parallel to the fiber axis, the crystallites align until their movement is restricted by the misoriented crystallites. If there is sufficient stress, the misoriented crystallites will rupture. When the size of the ruptured crystallites (perpendicular to the fiber axis) is larger than the critical flaw size, crack propagation leads to catastrophic failure, *i.e.* the fiber breaks.

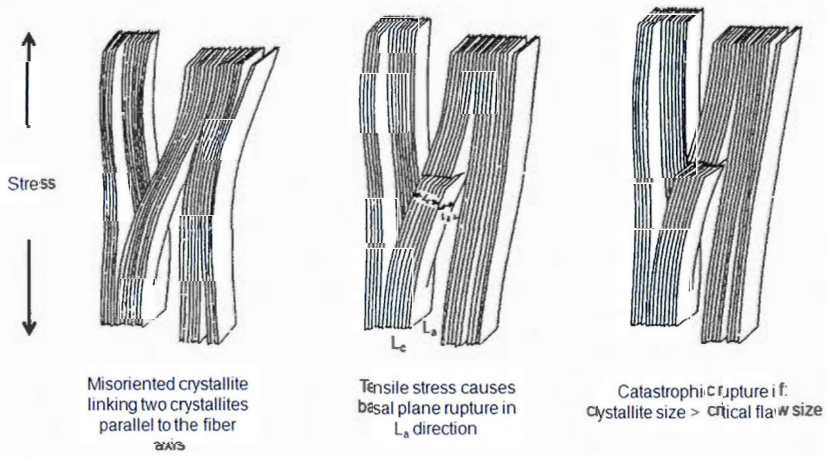



**Figure 1.13** Reynold and Sharp's mecanism for tensile failure of PAN based carbon fibers [8, 9].

## 1.6 Carbon fiber / Composite market

In the past decade, the use of thermoset structural composites, and more specifically carbon fibers reinforced plastics (CFRPs), increased significantly in aerospace with the development of the Boeing 787 Dreamliner and the Airbus A380 programs containing approximately 50 wt. % and 20 wt. % of CFRPs respectively [7, 12]. They are also being incorporated in a multitude of other products, such as sailboats and consumer goods. Annual

global sales of CFRPs were $13.6 Billion in 2010, and will increase to over $25 Billion by 2025 [13].

The carbon fiber market has been growing at a steady rate of 10 to 15 % annually [7]. In 2011, the global demand of carbon fiber tow rose to 45,800 tons. The aerospace industry accounted for 6,410 tons representing approximately 15 % of the carbon fiber market [14]. Carbon fiber demand by year and industry is depicted graphically in Figure 1.14 [15].

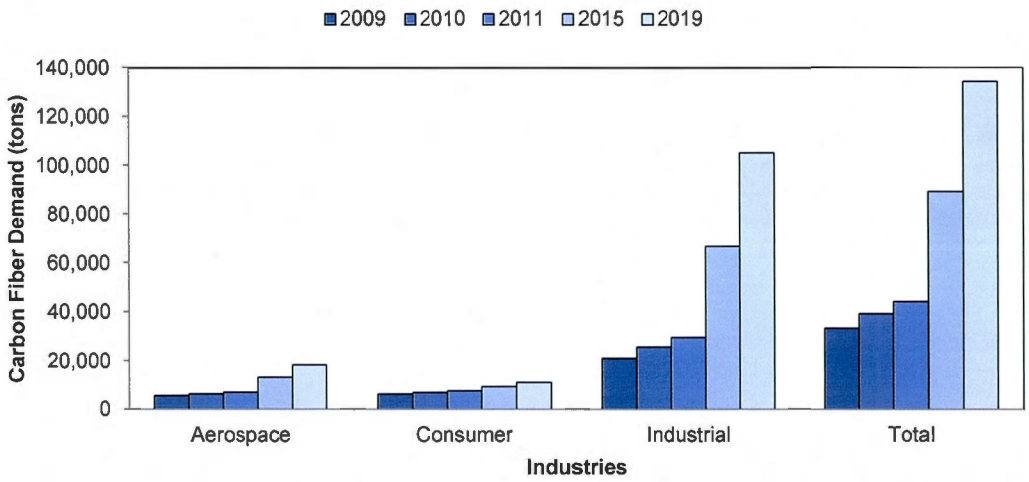



**Figure 1.14** Carbon fiber demand by year and industry [15].

## 1.7 The need to recycle

Although thermoset structural composites present numerous advantages, their increasing use generates a significant amount of composite waste estimated at 3,000 tons per year in North America and Europe [16]. This waste includes out-of date prepregs, manufacturing cut-offs, testing materials, production tooling and end-of-life components [12, 17]. Additionally, 8,500 commercial aircrafts will be decommissioned by 2025, containing approximately 20 tons of CFRPs per aircraft [12]. Currently, the vast majority of composite waste is sent to landfills, raising questions about waste generated from manufacturing and at end-of-life, especially in the aircraft industry.

Environmental concerns have lead to strict management conditions with respect to composite waste, especially in the European Union (EU). Since 2004, the Landfill Directive (1999/31/EC) [18] has rendered the disposal of composite waste to landfills illegal in many EU countries. Meanwhile, extended producer responsibility has set recycling targets for many types of waste. One important example is the end of life vehicle directive (2000/53/EC) [19], which states that after 2015; only 5 wt. % of an end-of-life vehicle can be sent to landfills. In North America, there is currently no legislation to curtail composite waste disposal. However, a few developments have recently been made by certain provincial governments, such as the province of Quebec (Canada), which has increased landfilling fees. A detailed analysis of composite waste legislation is provided for in the appendix. The increasing legislation on composite waste management requires the establishment of recycling routes to ensure proper conformity with upcoming regulations.

In addition to the legislative "push" factor, another driving force for recycling thermoset structural composites is recovering recycled carbon fibers, which requires approximately 10 times less manufacturing energy than virgin carbon fibers [12].

## 1.8 Challenges

Thermoset structural composites are inherently difficult to recycle due to their complex composition; as they are a mixture of reinforcing fibers, polymer resin, as well as, additives or fillers. Moreover, they are often manufactured in combination with other materials. For example, they may contain honeycomb or foram cores to reduce weight, metal inserts to fasten onto other parts, and paint. Finally, in contrast to thermoplastics which can easily be re-melted, the cross-linked structure of thermosets prevents re-molding [12, 17].

## 1.9 Recycling strategies

### 1.9.1 Overview

There are two main technological families for thermoset structural composite recycling: mechanical grinding and fiber reclamation (Figure 1.15) [12, 20]. Mechanical grinding consists of breaking down scrap composites by shredding, crushing, or milling, and

then separating the fragments into powdered (rich in resin) and fibrous (rich in fibers) products that can be used as fillers in new composites, artificial woods, asphalt, cement and other applications. Fiber reclamation consists of employing either a thermal or chemical process to break down thermosetting resin, thereby freeing the fibers. Additionally, energy and chemicals can be recovered from the by-products. Fiber reclamation is the preferred method for recycling CFRPs because high quality recycled carbon fibers can be recovered, producing a potentially more valuable product. Virgin carbon fibers require 198-594 MJ / Kg of manufacturing energy, while recycled carbon fibers require only 11-36 MJ / kg [12]. Therefore, fiber reclamation will be the focus of this thesis, as it is the more economically viable process if applications can be found for recycled carbon fibers. The following sections will take a detailed look at different fiber reclamation techniques available for thermoset structural composites, and more specifically CFRPs.

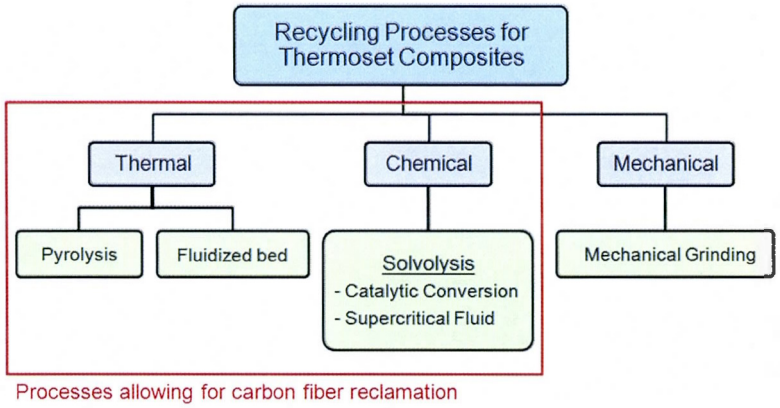



**Figure 1.15** Recycling strategies for thermoset structural composite waste [12, 20].

### 1.9.2 Pyrolysis Processing

Pyrolysis processing is currently the most mature method for recycling thermoset structural composites, as it can recover high quality recycled carbon fibers from a diverse feed stock [12, 20]. As shown in Figure 1.16, pyrolysis occurs when composite waste is heated to 450 °C – 700 °C in an inert environment [7, 12, 20, 21]. This inert environment prevents the oxidation of the fibers (susceptible to induce a reduction of their mechanical properties), as well as, the combustion of the resin matrix. The resin is allowed to completely

volatilize, thereby producing both liquids and gases composed of lower chained molecules that can be recovered as chemical feedstock or fuel [20, 22, 23]. The remaining solid is composed of fibers, fillers, char, metal inserts, etc. [7, 12, 20, 21].

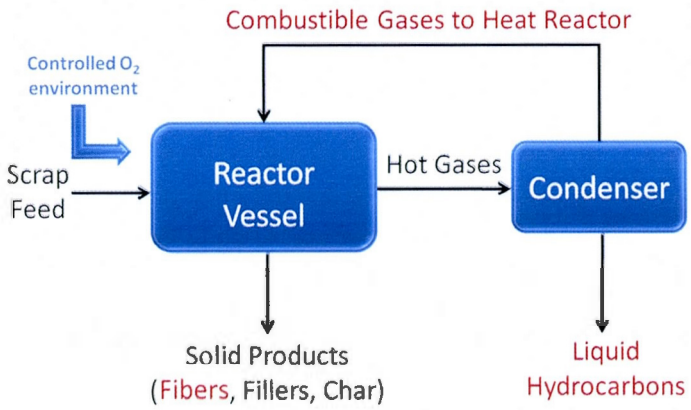



**Figure 1.16** A general process flow diagram for pyrolysis processing [20].

High pyrolysis temperatures (700 °C and up) may reduce the solid matter to char [21]. Consequently, the operating temperature is optimized to ensure the complete degradation of the resin matrix, while avoiding char formation on the surface of the fibers. The operating temperature depends primarily on the nature of the resin matrix. Polyester resins can fully decompose at a temperature of 450 °C, while other resins, such as epoxies or bismaleimides (BMI), need temperatures ranging from 500 °C to 550 °C [20, 22, 23]

Rather than operating in a completely inert environment, pyrolysis is usually carried out in a controlled oxygen environment because it offers the advantage of burning char and other contaminants off the surface of the fibers [12]. As long as the oxygen content is kept to a minimum, the fibers should not degrade. Furthermore, after pyrolysis, if there is any remaining char or resin present on the surface of the fibers, a quick oxidation step (increase of the oxygen level within the reactor) can be performed [12].

According to Pickering, recycled carbon fibers reclaimed by pyrolysis processing show little to no degradation in their mechanical properties (< 5 %) [17]. However, temperature, oxygen concentration, and residence time in the reactor can greatly affect their properties. As mentioned previously, char formation may occur on the surface of the fibers, which would affect their ability to bond to a new resin matrix [12].

Torres *et al.* [23] carried out pyrolysis experiments ranging from 300 °C to 700 °C on Sheet Molding Compounds composed of polyester and glass fibers. Pickering carried out pyrolysis experiments ranging from 350°C to 800 °C on various composites, including thermoset and thermoplastic resins, as well as glass and carbon fibers [20].

Torres *et al.* [23] found that there was no significant change in the composition and gross caloric value (GCV) of the pyrolysis by-products from 400 °C to 700 °C (Table 1.1). GCV is defined as the energy released as heat when a compound undergoes complete combustion with oxygen under standard conditions [24]. The gaseous product was mainly composed of CO, $CO_2$, and $C_{1-4}$ hydrocarbons with a GCV of 14 MJ / $m^3$. This energy is sufficient to fuel the reactor which would make the process self sustaining. Additionally, CO and $CO_2$ can be re-introduced into the reactor to provide an inert environment. The liquid product ($C_{5-20}$ hydrocarbons) was similar in composition to diesel and had a GCV of 37 MJ / kg; therefore, it can be used as either chemical feedstock or fuel. Pickering yielded very similar results. However, he found that epoxy resins produced a gas rich in methane, which substantially increased the GCV to 43 MJ / kg [20].

**Table 1.1** Characterization of the liquid and gas pyrolysis products from sheet molding compounds composed of polyester and glass fibers [23, 24].

| Pyrolysis Products | Proportion (wt.%) | Gross Caloric Value (GCV) |
|---|---|---|
| **Solids** | 70 | - |
| **Liquids:**<br>Aromatics (66 wt.%)<br>Oxygenated compounds (25 wt.%)<br>Others (9 wt.%)<br>*[Similar in composition to diesel]* | 15 | 37 MJ/kg<br>*Ethanol: 30 MJ/kg*<br>*Diesel : 45 MJ/kg*<br>*Gasoline: 58 MJ/kg*<br>Note: Can be used as either chemical feedstock or fuel. |
| **Gases:** | 15 | 14 MJ/$m^3$ |

| | | |
|---|---|---|
| CO (60 vol.%)<br>$CO_2$ (30 vol.%)<br>$C_{1-4}$ (10 vol.%) | | *Hydrogen: 13 MJ/m$^3$*<br>*Natural gas: 43 MJ/m$^3$*<br>*Butane: 133 MJ/m$^3$*<br>Note: Sufficient to fuel pyrolysis reactor. |

### 1.9.3 The Fluidized Bed Process

For the past 15 years, the University of Nottingham has worked on the development of a laboratory scale fluidized bed process, capable of recovering both glass and carbon fibers from thermoset structural composite waste [12, 17, 20, 25]. This process is particularly suitable for end-of-life components because it can treat heavily contaminated materials. The fluidized bed process consists of a fast thermal oxidative decomposition of the resin matrix, which allows for the recovery of fibers, fillers, metals, etc. [12, 17, 20, 26]. As shown in Figure 1.17, this process requires three main units / steps: the fluidized bed reactor, the fiber and filler separation step, and the secondary combustion chamber [26].

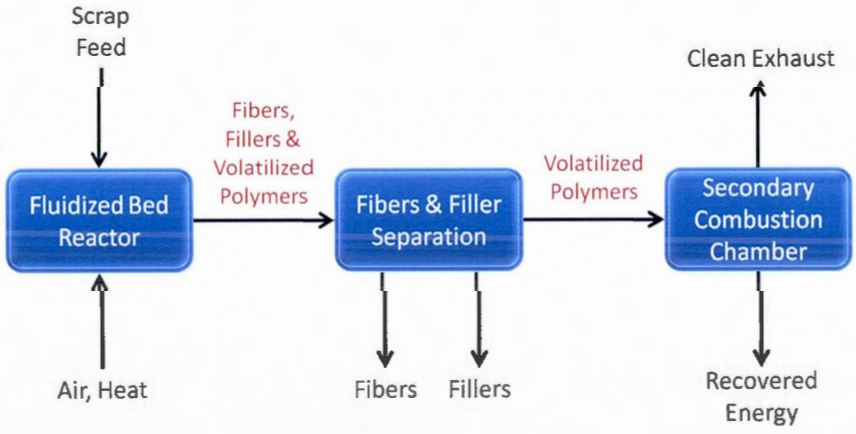



**Figure 1.17** A general process flow diagram for the fluidized bed process [26].

In the fluidized bed reactor, a stream of hot air with a velocity of 0.4 m / s to 1.0 m / s is used to fluidize a bed of silica particles approximately 0.85 mm in size [20]. The composite

waste is fed into the fluidized bed. Due to the high operating temperature and the oxidative atmosphere, the resin volatilizes and partially combusts, allowing for natural segregation to occur: heavier metallic components sink in the bed, while fibers and fillers are carried away by the gas stream [20, 26]. A schematic of the fluidized bed reactor is shown on Figure 1.18.

The two key parameters affecting the quality of the fibers are the operating temperature and the residence time. The operating temperature depends primarily on the nature of the resin matrix; polyester resins can fully decompose at a temperature of 450°C [26], while other resins, such as epoxies, need higher temperatures from 500-550°C [12, 20]. The residence time must be kept to a minimum to avoid severe degradation of the fibers. This is achieved by reducing the size of the scrap composite feed to about 25 mm x 25 mm before entering the reactor [20, 26].

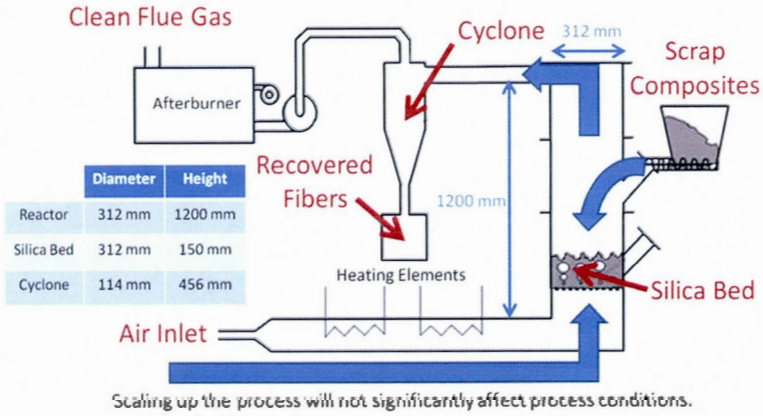



**Figure 1.18** A schematic of the fluidized bed reactor [17, 25-27].

The gas stream exiting the reactor is a mixture of fibers, fillers and volatilized polymers. Separating the high value recycled carbon fibers from the relatively low value fillers and polymers can be achieved by using a rotating sieve separator and a cyclone. The rotating sieve separator consists of a rotating mesh that captures long fibers and allows short fibers and fillers to pass through, while a cyclone is used to separate the short fibers from the fillers. The recycled carbon fibers are collected and washed in an aqueous solution that may contain sizing [26].

The volatilized polymers exiting the reactor are not fully combusted. Therefore, to prevent the release of contaminants in the atmosphere, a secondary combustion chamber burns the volatilized polymers to produce a clean flue gas. It operates at a temperature of 1000 °C and is capable of recovering approximately 16 MJ / kg of energy [26].

According to Pickering, the fluidized bed process is capable of recovering recycled carbon fibers with 25 % to 50 % loss in tensile strength and no reduction in tensile modulus [17]. Moreover, they have similar surface properties to virgin carbon fibers, and are completely free of resin and char [25]. They typically have a length comprised between 6 mm and 10 mm, and are in a `fluffy` form.

### 1.9.4 Catalytic Conversion

Allred *et al.* [12, 27] and Gosau *et al.*[12, 28] have developed a catalytic conversion process to recycle a wide variety of composites, including both thermoplastic and thermoset matrices, focusing mainly on aircraft parts and electronic assemblies. This process is capable of handling a diverse waste stream and does not requires any pre-sorting before treatment. This tertiary recycling process uses a liquid catalyst to degrade the resin into lower molecular weight hydrocarbons that can then further reclaimed as fuel or chemicals. After separating the hydrocarbons, metals, fillers, and fibers can be reclaimed for reuse or disposal. This process operates at low temperatures and pressures, typically at 150°C / 150 psi [7, 27, 29]. Figure 1.19 depicts a general process flow diagram for the catalytic conversion process.

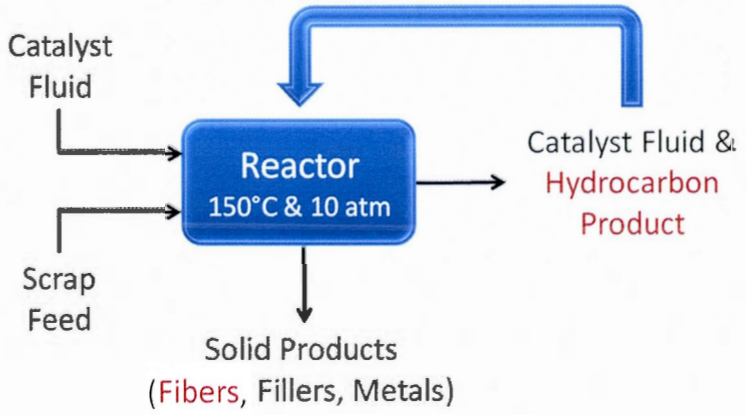



**Figure 1.19** A general process flow diagram for the catalytic conversion process [17].

According to Pickering, the catalytic conversion process is capable of recovering high quality recycled carbon fibers with minimal degradation in tensile strength (1 % to 17 %) [17]. The recycled carbon fibers have similar surface properties to virgin carbon fibers, and are completely free of resin.

The hydrocarbon product leaves the reactor mixed with the liquid catalyst. A certain percentage is cycled back into the reactor, while the remainder is separated and recovered [28]. Shredded composite waste from damaged F/A-18 horizontal stabilizers was recycled using the catalytic conversion process. As shown in Table 1.2, the hydrocarbon product recovered from this waste is mostly composed of phenolics.

**Table 1.2** Chemical composition of hydrocarbon product recovered from catalytic conversion [29, 31].

| **Compound** | **Proportion (wt.%)** | **Gross Caloric Value (GCV)** | |
|---|---|---|---|
| Phenol | 67 | 33 MJ/kg | *Ethanol: 30 MJ/kg*<br>*Diesel : 45 MJ/kg*<br>*Gasoline: 58 MJ/kg* |
| Toluene | 7 | 41 MJ/Kg | |
| Other (Mostly Phenolic derivatives) | 26 | - | |

### 1.9.5 The Supercritical Fluid Process

The supercritical fluid process is a new and promising technology that can convert polymeric waste back into monomers or petrochemical feedstock [30]. It consists of mixing a reactive medium with the thermoset structural composite waste, causing the resin matrix to decompose and dissolve, thereby freeing the fibers. Supercritical fluids possess unique properties exhibiting both liquid and gas behaviour (low viscosity, high mass transport coefficient and high diffusivity) [31].

Supercritical alcohols (methanol, ethanol, n-propanol) and acetone have received much attention as a reactive media since they are readily available, relatively inexpensive and able to dissolve many organic and inorganic compounds. They also have low critical pressures ($P_c$) and high critical temperatures ($T_c$) making them ideal for the breakdown and extraction of organic materials. n-propanol ($P_c$ = 5.2 MPa; $T_c$ = 241°C) [31] has a high solubility with organic materials and is relatively benign, thus making it an ideal candidate [32]. Alkali catalysts, such as NaOH, KOH, CsOH, may be added to speed up the decomposition rate [17, 31]. A general process flow diagram of the supercritical fluid process is shown on Figure 1.20. This is a solvolytic process; a solvent is used to break up the polymer matrix, thereby freeing the reinforcing fibers. The reactor operates at 5 MPa and 310-500°C. [31]

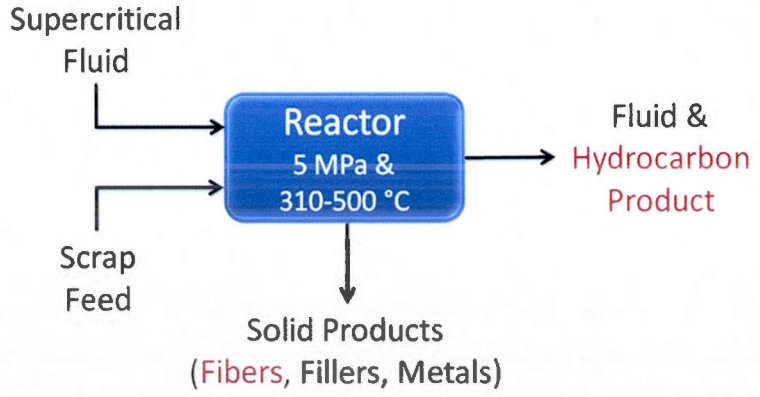



**Figure 1.20** A general process flow diagram for the supercritical fluid process [17, 33].

Piñero-Hernanz *et al.* [33] recycled thermoset structural composites using batch and semi-continuous supercritical fluid processes. The batch process was found to be inefficient, as it is limited by mass transfer: as the polymer concentration increases in the supercritical fluid; its solubility drops until the supercritical fluid can no longer dissolve the resin matrix. Therefore, a semi-continuous system is preferred.

Currently, only laboratory scale set-ups have been tested. Larger scale demonstrations are needed to further assess the viability of using the semi-continuous supercritical fluid process to recover recycled carbon fibers from thermoset structural composites [17].

According to Pickering, the semi-continuous supercritical fluid process is capable of recovering high quality recycled carbon fibers with little to no reduction in tensile properties (< 3 %) [17, 32]. Furthermore, the surface of the fibers is clean and exhibits good bonding with epoxy resin.

The supercritical fluid process decomposes epoxy resin into phenolic based compounds as shown in Table 1.3 [17].

**Table 1.3** Chemical composition of decomposed polymers produced by the semi-continuous supercritical fluid process [17].

| Chemical Species | Composition (wt.%) |
|---|---|
| Phenol | 34.9 |
| p-isopropylphenol | 26.4 |
| p-isopropenylphenol | 18.1 |
| m-methylphenol | 6.5 |
| m-ethylphenol | 4.7 |
| Other | 9.4 |

### 1.9.6 Other Available Technologies

Various other technologies have been studied to recycle thermoset structural composites. However, they proved to be unsuccessful or difficult to scale-up. Microwave treatment, for example, is capable of recovering high quality recycled carbon fibers from thermoset structural composites but its scalability is an obvious issue [34]. Examples of

unsuccessful treatment methods include chemical treatment, molten salt treatment, and thermal shock treatment [35, 36].

## 1.10 Re-manufacturing Carbon Fiber Reinforced Thermoset Composites

### 1.10.1 Overview

Recycled carbon fibers recovered by any of the above mentioned methods are in chopped form; therefore, they will have to be used as discontinuous reinforcement in new composite materials [12, 17]. However, reintegrating chopped recycled carbon fibers in new resin matrices poses several challenges, as most manufacturing processes are designed for dry reinforcements available as continuous fibers or woven fabrics.

There are several options for producing thermoset composites containing chopped recycled carbon fibers [6, 7, 12]. The following techniques will be will be discussed in detail later on in this chapter. Recycled carbon fiber mats can be fabricated by either a wet-lay process [37] or by carding, and then impregnated with a resin system by either wet lay-up, or by liquid molding processes, which includes resin transfer molding (RTM) or infusion / compression molding. Another option would be to use sheet molding compound (SMC), where chopped recycled carbon fibers and resin paste in B-stage are mixed beforehand, and then undergo compression molding to form the final composite piece. Finally, thermoplastics can also be produced by mixing recycled carbon fibers and thermoplastic resin in an extruder, producing pellets that can then be re-melted and shaped into a composite piece by injection molding. This discussion will be limited to re-manufacturing carbon fiber reinforced thermoset composites.

### 1.10.2 Fabricating Recycled Carbon fiber Mats

Recycled carbon fiber mats can be produced by either a wet lay process (Figure 1.21) or by carding. The wet-lay process [37] is commonly used for making paper, and is well suited for making recycled carbon fiber mats. The fibers are agitated and dispersed in the mixing tank. The mixture is then pumped into the headbox, where a vacuum sucks the fibers onto an inclined conveyor screen (forming wire), while simultaneously removing excess

water. Finally, the fibers in the resulting mats are binded together and dried in an oven. Generally, fibers lay randomly onto the screen, however, they can be preferentially oriented in the direction of the travelling conveyor screen by increasing the belt speed.

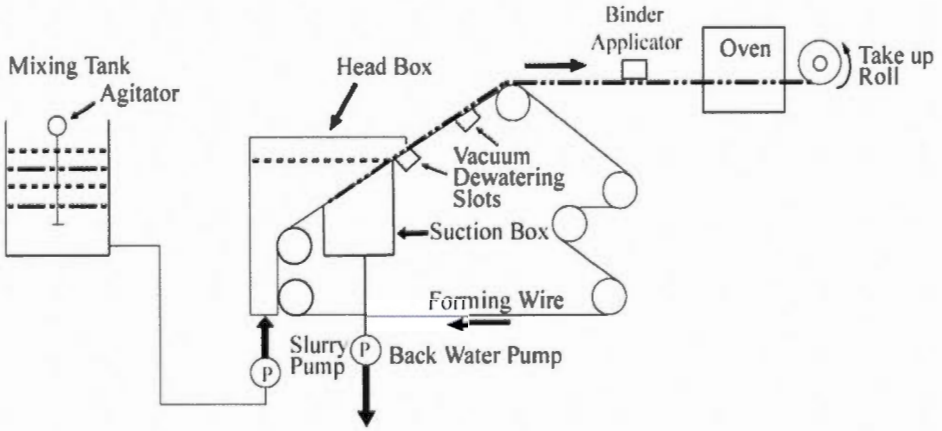



**Figure 1.21** Wetlay Process for making recycled carbon fiber mats [39].

Carding is a mechanical process that disentangles, cleans and intermixes fibers to produce a continuous web suitable for yarn production. Generally, this process is used for natural fibers such as cotton or wool. In this work, a roto-carder (Figure 1.22) produced recycled carbon fiber mats by separating, interlocking and partly aligning recycled carbon fibers.

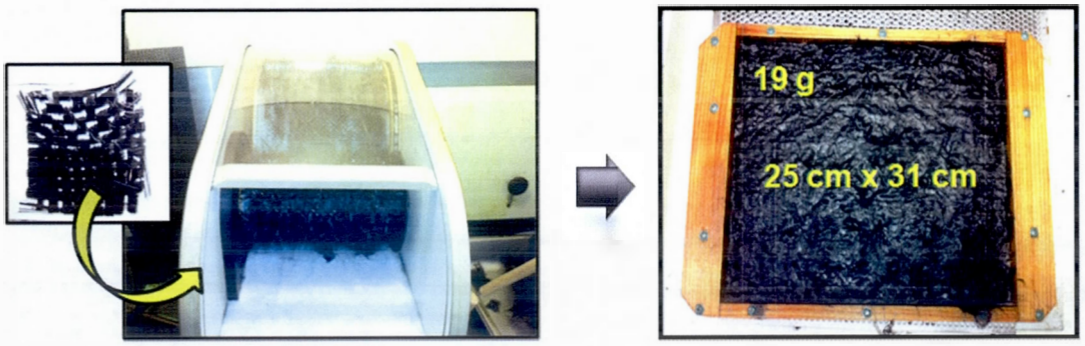



**Figure 1.22** Carding process for making recycled carbon fibers mats

1.10.3 Wet lay-up processing

As depicted in Figure 1.23, wet lay-up processing consists of laying a recycled carbon fiber mat into a mold, and saturating it with liquid resin. Rollers can then be used to spread the resin uniformly into the mat, thus reducing the void volume. Additional layers of mat and resin can be laid onto one another until the required composite thickness is reached. The assembly is finally cured at room temperature or in an oven. This is a very simple method to produce recycled carbon fiber reinforced thermoset composites; however, it is generally very difficult to control the uniformity of the piece, as there is little control on the resin content.

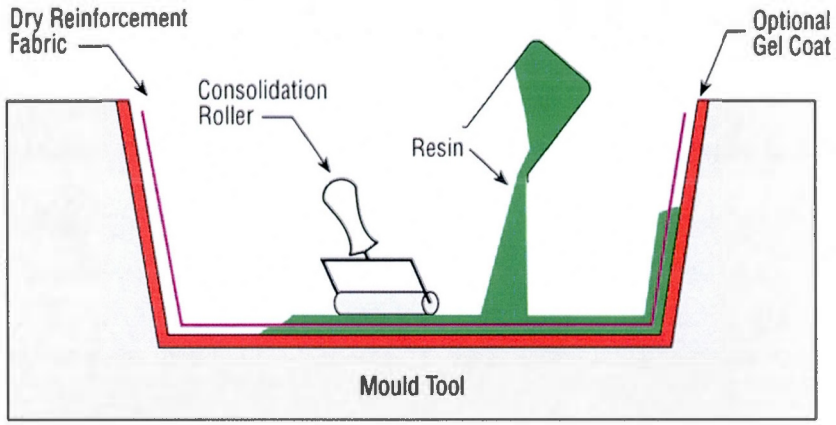



**Figure 1.23** A schematic representation of the wet-lay process [6].

### 1.10.4 Resin Transfer Molding

Resin transfer molding (RTM) is schematically depicted in Figure 1.24. Recycled carbon fiber mats are stacked up and compacted into a mold. The mold is then pre-heated to the cure temperature, and the mats are subsequently impregnated by injecting resin at high pressures at the inlet position. At the outlet position, vacuum can be applied to help the resin to flow into the mat. Once fully impregnated, the resin is cured. RTM allows the fabrication of composite parts with high fiber volume fraction (up to 60 wt. %), consistent quality, and low void volumes. However, if the permeability of the mats is too low, RTM cannot be used as the required injection pressures become too high.

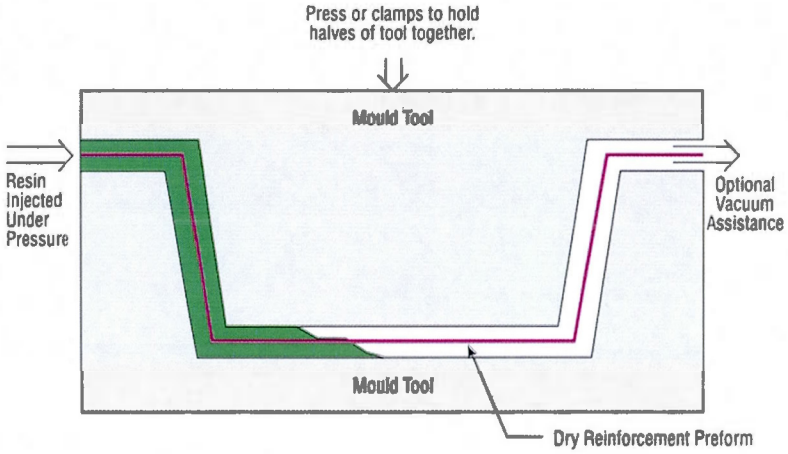



**Figure 1.24** A schematic representation of Resin Transfer Molding (RTM) [6].

### 1.10.5 Infusion Molding

A schematic of the infusion process is given in Figure 1.25. The system consists of a mold tool on the bottom, the recycled carbon fiber mats in between, and a flexible membrane (vacuum bag) on top. The resin is infused into the mats by applying vacuum to the system. Once fully impregnated, the resin is either cured in an oven or undergoes compression molding for further compaction. Infusion molding allows for the fabrication of composite parts with fiber volume fraction up to 55 wt. %, if adequate compaction is achieved. This process is less expensive than RTM, and provides better quality parts than the wet lay-up process. However, controlling the resin uniformity can be difficult, leading to resin rich areas in the corners or at the edges of the final composite piece.

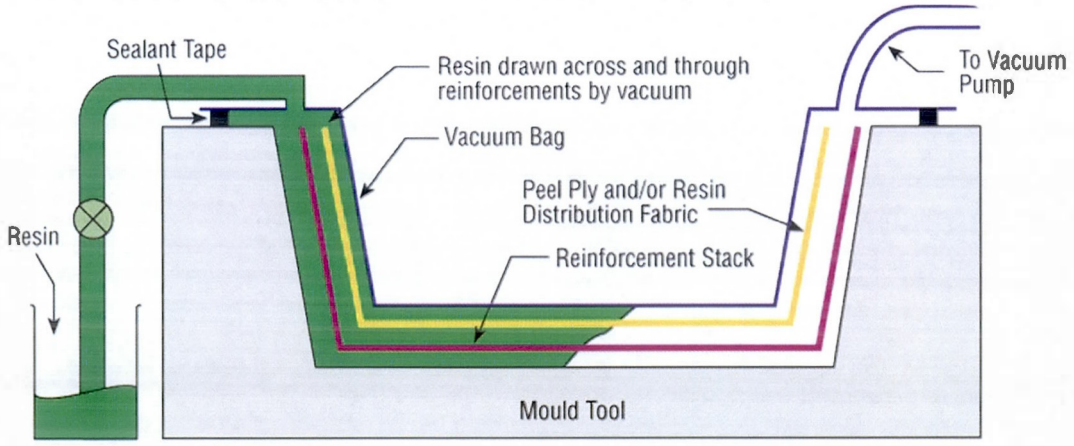


**Figure 1.25** A schematic representation of infusion molding [6].

### 1.10.6 Sheet Molding Compound (SMC)

A schematic of the SMC process and compression molding is given in Figure 1.26 and Figure 1.27. SMC sheets are a semi-finished product made from chopped recycled carbon fibers and resin paste in B-stage (B-stage is an intermediate stage in a thermosetting resin reaction in which the polymer softens but does not fuse when heated, and swells but does not dissolve in contact with certain liquids). They are obtained by passing chopped recycled carbon fibers and resin through compaction rollers forming a sheet. The resulting SMC sheets are the placed into a mold, and compression molded. The SMC process can be highly automated to increase production rate. Moreover, it allows for the production of composite parts with fiber volume fractions up to 55-60 wt. %, and low void volumes. However, formulation and compounding of the SMC sheets from the raw materials (fibers and resin) is challenging.

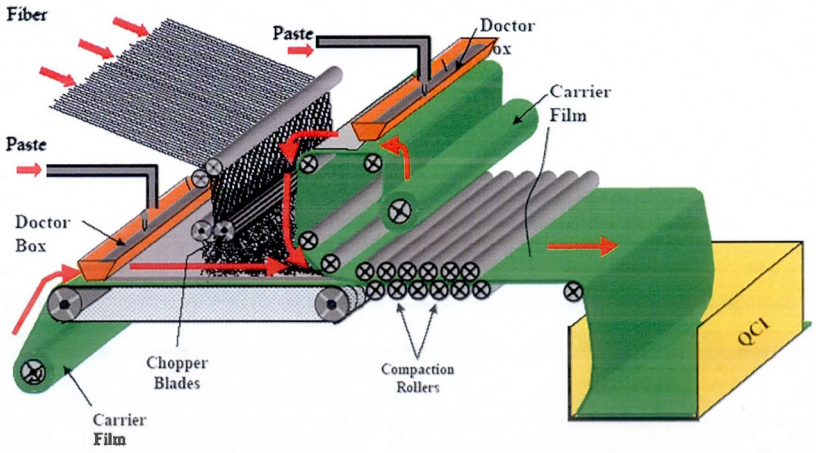



**Figure 1.26 Schematic representation of the SMC process [7].**

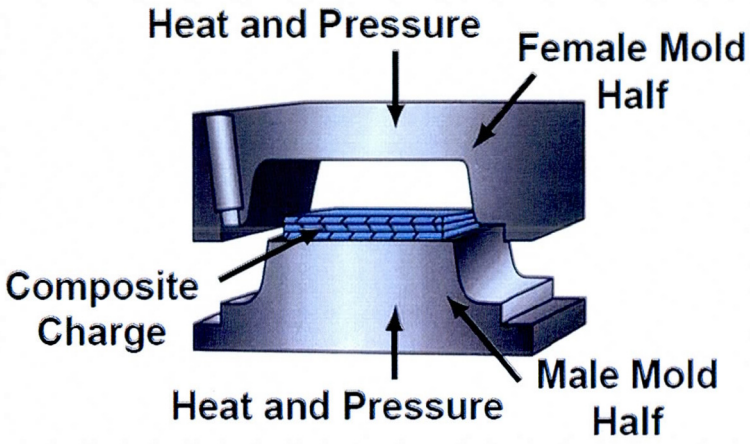



**Figure 1.27** Schematic Representation of Compression Molding [7].

## 1.11 Summary

The economic viability of recycling carbon fiber reinforced thermoset composite waste depends on the ability of recovering high quality recycled carbon fibers. Thermoset composites can then be re-manufactured using these recycled carbon fibers. In this work, recycled carbon fibers were recovered from thermoset composite waste generated by the Canadian aerospace industry, using Materials Innovation Technologies commercial scale pyrolysis process. In this work, recycled carbon fibers were recovered from thermoset composite waste generated by the Canadian aerospace industry, using Materials Innovation Technologies commercial scale pyrolysis process. In this work, recycled carbon fibers were recovered from thermoset composite waste generated by the Canadian aerospace industry, using Materials Innovation Technologies commercial scale pyrolysis process. Chapter II assesses the effect of pyrolysis processing on the morphological, mechanical and surface properties of the recycled fibers by evaluating and comparing them to a virgin fiber reference. The properties of the recycled fibers were found to be suitable for composite consolidation, and thus, Chapter III covers the fabrication of epoxy / recycled carbon fiber plates, as well as, an evaluation of their morphology and mechanical properties. The recycled fiber composites were found to have excellent mechanical properties when compared to pure epoxy, and comparable properties to a virgin equivalent. Therefore, the potential of reintegrating recycled carbon fibers as reinforcement in new thermoset composites for a variety of applications has been demonstrated.

CHAPITRE II

# EFFECT OF MORPHOLOGICAL, MECHANICAL AND SURFACE PROPERTIES ON THE WETTABILITY AND INTERFACIAL ADHESION OF RECYCLED CARBON FIBERS*

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## 2.1 Abstract

Chopped recycled carbon fibers from prepreg and tooling were recovered from carbon fiber reinforced thermoset composite waste generated by the Canadian aircraft industry, using Materials Innovation Technologies commercial scale pyrolysis process. The objective was to analyze the effect of pyrolysis processing on the morphological, mechanical, and surface properties of recycled carbon fibers, and to determine how their synergistic interactions affected wetting and interfacial adhesion with epoxy resin. Recycled carbon fibers were characterized by: scanning electron microscopy, density measurements by pycnometry, micro-tensile testing, BET analysis, x-ray photoelectron spectroscopy, wettability analysis by dynamic contact angle measurement and interfacial adhesion with epoxy resin by micro-droplet testing. The results indicate that pyrolysis processing altered the surface properties of the recycled carbon fibers by effectively removing sizing and resin, thereby revealing surface topographies. Wetting and interfacial adhesion between the surface of recycled carbon fibers and epoxy resin were found to be predominantly affected by Lewis acid / base interactions of oxygenated surface functional groups, as well as, by mechanical interlocking. Mechanical interlocking appeared to be the more important parameter, as the striated prepreg fibers out-performed the smooth tooling fibers in micro-droplet testing regardless of the chemical surface properties.

## 2.2 Introduction

The use of carbon fiber reinforced thermoset composites has doubled in the last decade, generating a significant amount of waste, estimated at 3,000 tons per year in North America and Europe [1]. As a result, major users like aircraft manufacturers are under pressure to reduce waste through recycling or reuse, affecting both in-process waste and end-of-life disposal. Fiber reclamation has gained momentum because of its ability to recover high quality carbon fibers by employing either a thermal or chemical process to break down thermosetting resin [2, 3]. The most common fiber reclamation method is pyrolysis processing [2-4], defined as the thermal degradation of organic material in a controlled oxygen environment. Other fiber reclamation technologies include catalytic conversion [3, 5, 6], fluidized bed reactor [2, 3, 7, 8] and supercritical fluids [9, 10].

Recycled carbon fibers have already been reintegrated as reinforcing fibers in new polymer composites [2, 3, 11-13], however, further optimization of their mechanical performance requires better knowledge of the fiber / resin interface. Interfacial properties can be characterized by wettability and interfacial adhesion. Complete wetting is a prerequisite for good adhesion because it prevents the formation of voids; while, good adhesion is essential for stress transfer between fiber and resin, as it is well correlated with the interlaminar shear strength (ILSS) of composite materials [14-16].

Several studies [2, 3, 17-19] have reported that recycled carbon fibers retained their morphological and mechanical properties, however, pyrolysis processing altered their surface properties by removing resin and sizing, and altering the distribution of oxygenated surface functional groups. These functional groups play an important role in wetting and interfacial adhesion, as they interact through Lewis acid / base interactions with epoxy resin [14, 15]. Yet, the Lewis acid / base surface characteristic of recycled carbon fibers has not been thoroughly investigated.

In this study, chopped recycled carbon fibers were recovered from carbon fiber reinforced thermoset composite waste generated by the Canadian aircraft industry, using Materials Innovation Technologies commercial scale pyrolysis process. The objective was to

analyze the effect of pyrolysis processing on the morphological, mechanical, and surface properties of recycled carbon fibers, and to determine how their synergistic interactions affected wetting and interfacial adhesion with epoxy resin. Morphology was probed by Scanning electron microscopy, while their mechanical performance were assessed by micro-tensile testing. Surface properties were probed by BET analysis, x-ray photoelectron spectroscopy, wettability study by dynamic contact angle analysis, and interfacial adhesion by micro-droplet testing with epoxy resin.

## 2.3 Materials

### 2.3.1 Carbon Fibers

Recycled carbon fibers were recovered from a 100 kg sample of carbon fiber reinforced thermoset composite waste generously donated by Bell Helicopter Textron Canada Ltd. (BHTCL: Mirabel, Quebec, Canada). This sample was composed of actual waste generated by the Canadian aerospace industry. It contained carbon fiber prepregs (cured and uncured) based on epoxy and bismaleimide resins, and tooling parts made from carbon fiber reinforced epoxy resin with trace amounts of silicone. Pyrolysis processing was performed at Materials Innovation Technologies (MIT: Lake City, South Carolina, United States) using their commercial scale batch pyrolysis oven. Before pyrolysis, the waste was sorted and cut into 2.5 cm x 2.5 cm fragments to limit the fiber length distribution, thereby controlling the overall uniformity of the recycled fibers. Pyrolysis was performed at low temperatures (< 400 °C) under a controlled atmosphere, and the residence time was adjusted as a function of the material to be pyrolyzed. Recycled carbon fibers were obtained from prepregs and tooling. As the recycled fibers originate from different feedstock, they are composed of various types of carbon fibers. Hence, it was not possible to precisely evaluate the effect of recycling on their properties. Therefore, the performance of the recycled fibers was compared to Torayca@ T700S (Toray fibers: sized, tensile modulus: 230 GPa, tensile strength: 4,900 MPa), aerospace grade virgin carbon fibers from Toray (Flower Mound, TX, USA). For BET analysis, Panex® 35 (Panex fibers: unsized, chopped to a length of 6 mm), industrial grade virgin carbon fibers from Zoltec (St. Louis, MO, USA) were selected, as they had an unsized surface. Upon visual inspection, the recycled fibers from prepreg had a woven structure and were cut into squares, while the recycled fibers from tooling were in a "fluffy" entangled

state. The Toray fibers, on the other hand, were spooled as a tow and subsequently cut into 2.5 cm lengths.

### 2.3.2 Resin

PRISM™ EP2400, an infusion grade epoxy system produced by Cytec Engineered Materials (Woodland Park, NJ, USA), was selected as the polymeric matrix for micro-droplet testing (Table 2.1).

**Table 2.1** Processing properties of the infusion grade epoxy PRISM™ EP2400 produced by Cytec Engineered Materials.

| Properties | PRISM EP™2400 |
|---|---|
| Injectable Temperature (°C) | 70 |
| Cure Temperature (°C) | 180 |
| Dry $T_g$ (room temperature, dry) | 179 |
| Wet $T_g$ (48 hour water boil, wet) | 163 |
| Toughness | Very High |
| Cured Resin Density (g/cm$^3$) | 1.24 |

## 2.4 Experimental

### 2.4.1 Characterization of Carbon Fiber Morphology

*Scanning Electron Microscopy*

Fiber morphology was probed by a Jeol GSM 840 scanning electron microscope (SEM) operating at 5 kV. Fiber diameters were measured using ImageJ software [20]. Reported values are the average of 5 samples for each fiber type.

*Fiber Density Measurement*

The recycled fiber density was measured with an InstruQuest Humipyc gas pycnometer (gas: helium, measurement pressure: 210 kPa ± 3 Pa, stabilization time: 300 s, temperature: 21.5 ° C, relative humidity: 17 %). Reported values are the average of 3 measurements.

### 2.4.2 Characterization of Carbon Fiber Mechanical Properties

*Micro-Tensile Testing*

Micro-tensile testing was performed on mono-filaments according to ASTM D3379 [21] using an Instron Microtester equipped with a 2N load cell. A gage length of 10 mm and rate of 1 mm / min were used. Reported values are the average of 30 samples for each fiber type. In all cases, error bounds represent the 95 % confidence limits for a student-t distribution.

### 2.4.3 Characterization of Carbon Fiber Surface Properties

*BET*

Carbon fibers were analyzed by adsorption isotherms of $N_2$ at 77 K. Quantachrome Instruments (Boynton Beach, FL, USA) Autosorb 1- MP equipment and software performed 20 point adsorption / 20 point desorption isotherms, 7 point BET for specific surface area determination, and pore size distribution analysis. Pore size was characterized according to IUPAC [22] as follows: micro-pores (< 20 Å), meso-pores ( > 20 Å and < 500 Å), and macro-pores ( > 500 Å).

*X-Ray Photoelectron Spectroscopy*

X-Ray Photoelectron Spectroscopy (XPS) analysis was performed using a Physical Electronics PHI 6500-ci with a Al standard anode (1486.6 eV) at 200 W for the survey spectra, and a Mg $K_\alpha$ (1253.6 eV) at 150 W for the high resolution spectra. No charge compensation was required. All spectra were recorded at a 45° take-off angle, and the area under analysis was 800 x 200 μm for all scans. The spectra were analyzed by CasaXPS software using an internal reference of 284.6 eV for the C 1s peak. Survey scans determined the surface elemental compositions, while the C 1s high resolution scans determined the concentration of oxygenated surface functional groups. The curve fitting procedure was described by Jiang *et al.* [7, 23].

*Wettability study by Dynamic Contact Angle Analysis*

A Dataphysics DCAT 11 Dynamic Contact Angle Meter and Tensiometer employing the Wilhelmy plate technique was used to measure contact angles using appropriate liquid

probes, which then characterize the Lifshitz - Van der Waal and Lewis acid / base contributions to the surface free energy of the carbon fibers [24]. Mass deflection was measured as the probe liquid was raised and lowered, measuring both the wetting and tear-off force according to the following relationship [15, 25]:

$$\cos\theta = \frac{mg}{P\gamma_l} \tag{2.1}$$

where $\theta$ is the contact angle, $m$ (g) is the mass deflection, $g$ is the gravitational constant (9.81 m / $s^2$), $P$ is the wetted fiber perimeter and $\gamma_l$ (mN / m) is the surface tension of the probe liquid.

Samples were prepared by gluing carbon fibers to a paper template that was suspended from a microbalance by a hook. Probing liquid was placed into a beaker that was held in place by a micrometer stage. The suspended sample was brought into contact with the liquid surface and subjected to one cycle of immersion at a speed of 100 μm / s and a depth of 3 mm. Mass deflection data were recorded at 5 Hz with a mass resolution of ± 10 μg. n-hexane was used to determine the average fiber perimeter, while 1-bromonaphthalene, water, and glycerol were used to characterize the surface free energy of the fibers. Reported values are based on 20 observations for each fiber type (5 replicates for each liquid probe).

*Micro-droplet Testing*

Micro-droplet testing [7, 23, 26] quantifies the interfacial shear strength (τ), i.e. the adhesion between the fiber and epoxy matrix. A normal force was applied on a micro-droplet of resin using shearing blades that pull the resin off the fiber. Assuming a cylindrical model, the interfacial shear strength was calculated by:

$$\tau = F/\pi D_f L \tag{2.2}$$

where $F$ is the debonding force, $D_f$ is the fiber diameter, and $L$ is the embedded length.

Samples were prepared by gluing the ends of a carbon mono-filament onto a 4 cm x 1 cm paper template with a punch hole through the middle. Elliptical epoxy droplets were applied onto the monofilament using a fine metal applicator connected to a heated soldering iron. Samples were cured in an oven for 2 hours at 180 °C. Droplets with embedded lengths varying between 20 μm to 50 μm were chosen for testing. Observations were made using a Nikon Eclipse 50i optical microscope connected to a QImaging Go-3 camera, and measurements were made using ImageJ software calibrated with a Pyser-SGI S8 stage micrometer graticule. A caliper attached to a Micos MT-65 linear stage served as shearing blades. The caliper opening was set to 10 μm and the speed was set to 0.1 mm / min. Force measurements were acquired using a Mettler Tolledo AB135-s/FACT balance connected to a computer using National Instruments LabView software. Reported values are based on 15 observations for each fiber type.

## 2.5 Results and Discussion

### 2.5.1 Characterisation of Carbon Fiber Morphology

SEM micrographs (Figure 2.1) revealed that the recycled fibers from prepreg and tooling were relatively undamaged, having no obvious cracks. Their diameters measured 6.5 ± 0.8 μm and 6.5 ± 0.9 μm respectively. Prepreg fibers exhibited surface striations designed to improve their adhesion with epoxy [7, 23], and residual resin was often observed, probably due to a lack of optimization of the pyrolysis process (the process was optimized for epoxy composites, whereas prepreg waste contained both epoxy and bismaleimide resins). Tooling fibers showed some loose debris and no surface striations. The Toray fibers, on the other hand, have a coating of sizing clearly visible on their surface, which is designed to improve adhesion with epoxy resin and protect the fibers against abrasion [14]. The average density of the prepreg fibers was determined by pycnometry to be 1.75 g / $cm^3$, close to the value of the Toray fibers (1.80 g / $cm^3$). Overall, the recycled fibers retained their bulk morphological properties summarized in Table 2; however, pyrolysis processing altered surface texture and chemistry by removing resin and sizing, thereby revealing their surface topographies.

a)

b)

c)

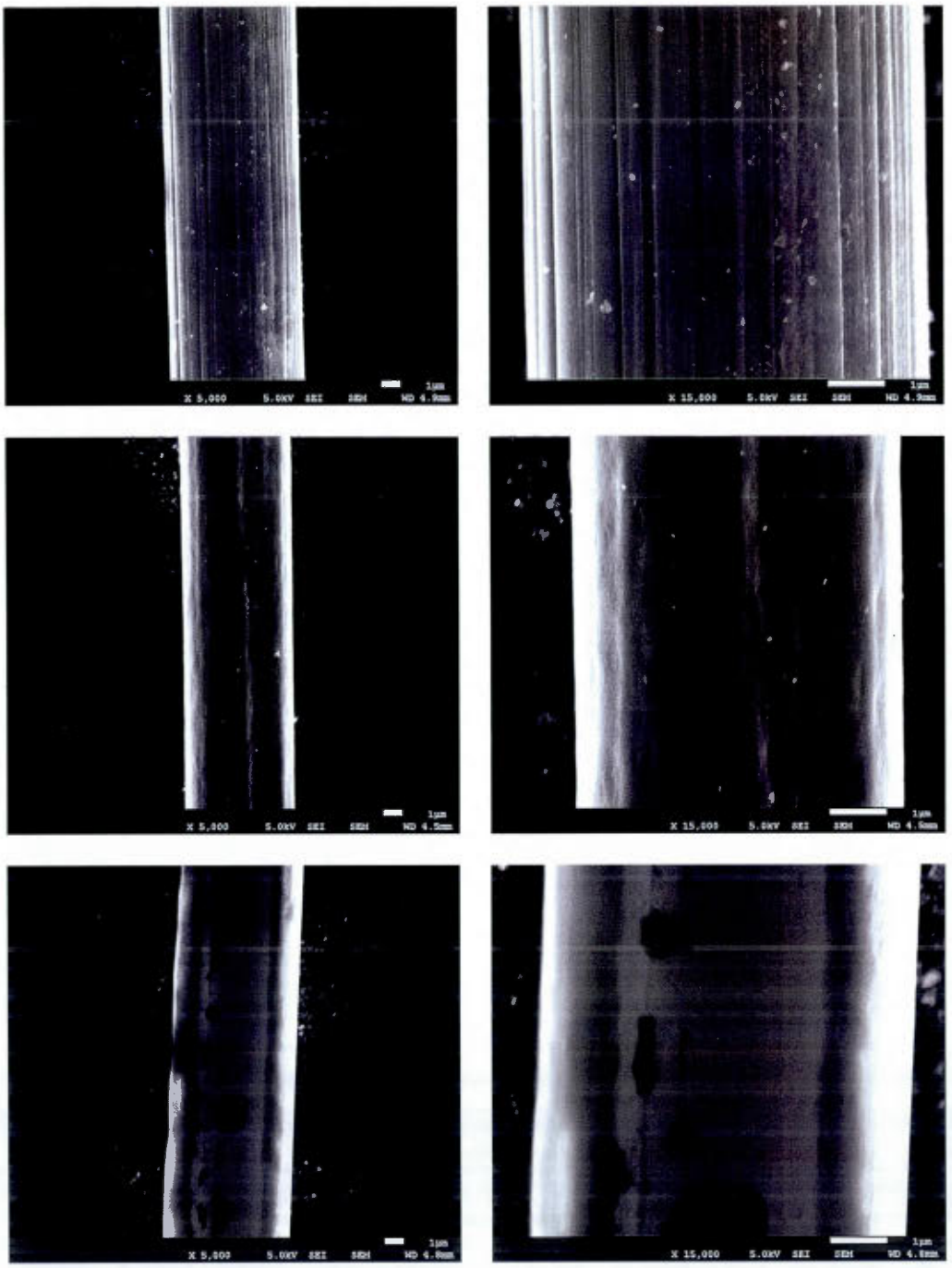


**Figure 2.1** SEM micrographs of the recycled carbon fibers from a) prepregs, b) tooling, and virgin carbon fibers from c) Torayca@ T700S.

**Table 2.2** Summary of carbon fiber morphology.

| Carbon Fiber Type | Diameter (μm) | Density ($g / cm^3$) | Surface Striations | Sizing |
|---|---|---|---|---|
| Recycled Fibers from Prepreg | 6.5 ± 0.8 | 1.75 | yes | no |
| Recycled Fibers fromTooling | 6.5 ± 0.9 | - | no | no |
| Torayca@ T700S | 6.5 ± 0.6 | 1.80* | -* | yes* |

* Torayca@ T700S Datasheet

2.5.2 Characterization of Carbon Fiber Mechanical properties

Micro-tensile testing was performed to determine the effect of pyrolysis processing on the mechanical performance of the recycled fibers. The recycled fibers from prepreg and tooling had a tensile modulus of 160 ± 20 GPa and 170 ± 10 GPa, and a maximum tensile strength of 3400 ± 400 MPa and 3800 ± 200 MPa, respectively (Figure 2.2). When compared to the Toray fibers, average differences of -10 % to - 5 % in tensile modulus and - 20 % to - 10 % in maximum tensile strength were observed. Tooling fibers offered a better mechanical performance than prepreg fibers, although prepreg composites contain high performance aerospace grades of carbon fibers, while tooling composites generally contain industrial grades of carbon fibers. This result may be due to process variations that can occur during recycling (possible degradation of the fiber surface). Therefore, further optimization of the pyrolysis conditions (temperature, residence time, and atmosphere), with respect to the type of composite waste being treated, should contribute to further improving the mechanical properties of the fibers. Overall, the recycled fibers retained their mechanical properties.

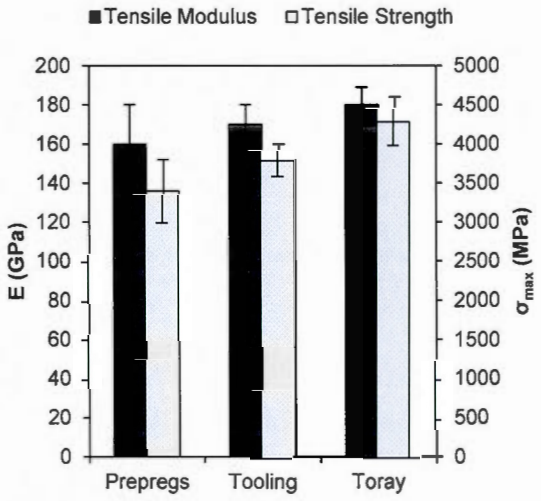



**Figure 2.2** Tensile modulus E (GPa) and maximum tensile strength $\sigma_{max}$ (MPa) of the carbon fibers.

### 2.5.3 Characterization of Carbon Fiber Surface Chemistry

Figure 2.3 displays the $N_2$ adsorption and desorption isotherms for the recycled fibers from prepreg and tooling. Both isotherms were of type II nature, indicating that the recycled fibers were non-porous solids [27]. In addition, very little hysteresis was observed between the adsorption and desorption isotherms, signifying that there were no large meso- or macro-pores (i.e. large cavities) present on their surface [27].

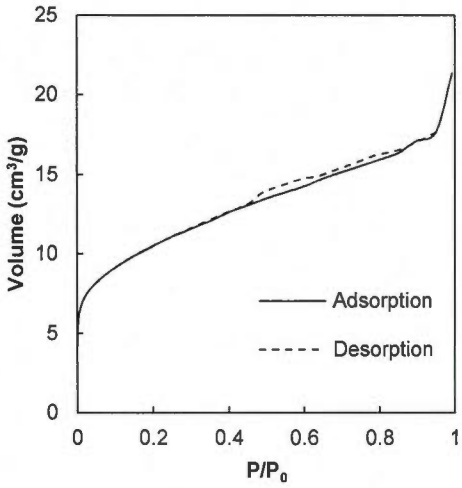
The recycled fibers were initially compared to the sized Toray fibers for BET analysis. However, sizing is a polymeric coating that can cover up surface defects, making it difficult to evaluate the effect of pyrolysis processing. Therefore, unsized Panex fibers were offered as a more appropriate comparison. 7 point BET analysis (Table 2.3) determined that the recycled fibers had a specific surface area approximately 9 times greater than the Toray fibers, and 43 times greater than the Panex fibers. Moreover, pore size distribution plots (Figure 2.4) established that this substantial increase was due to the introduction of many small pores (< 100 Å) on the surface of the recycled fibers. The presence of meso-pores on the Toray fibers was attributed to the uneven coating of sizing, while for the Panex fiber; it

was attributed to surface defects. Generally, an increase in the specific surface area of carbon fibers should improve interfacial adhesion between fiber and resin, as there is more intimate contact at the interface [15]. However, epoxy resin cannot penetrate such small pores [15], and subsequent micro-droplet testing shows this, as adhesion between the recycled and Toray fibers were quite similar. Therefore, BET analysis revealed that pyrolysis processing effectively removed sizing and resin, and slightly degraded the surface of the recycled fibers by the introduction of small pores, which had little effect on their interfacial properties with epoxy resin.

**Table 2.3** Specific surface area ($m^2/g$) of the carbon fibers.

| Fiber Type | Specific Surface Area ($m^2/g$) |
|---|---|
| Recycled Fibers from Prepreg | 43 |
| Recycled Fibers from Tooling | 43 |
| Torayca® T700S | 5 |
| Panex® 35 | 1 |

a)




b)

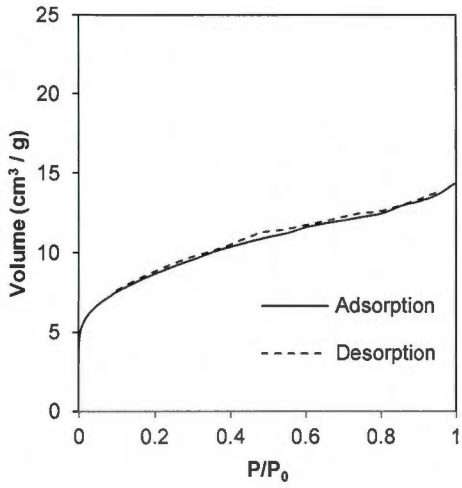



**Figure 2.3** 20 point $N_2$ adsorption / desorption isotherms. Volume ($cm^3/g$) versus relative pressure $P/P_0$ for the the recycled fibers from a) prepreg and b) Tooling.

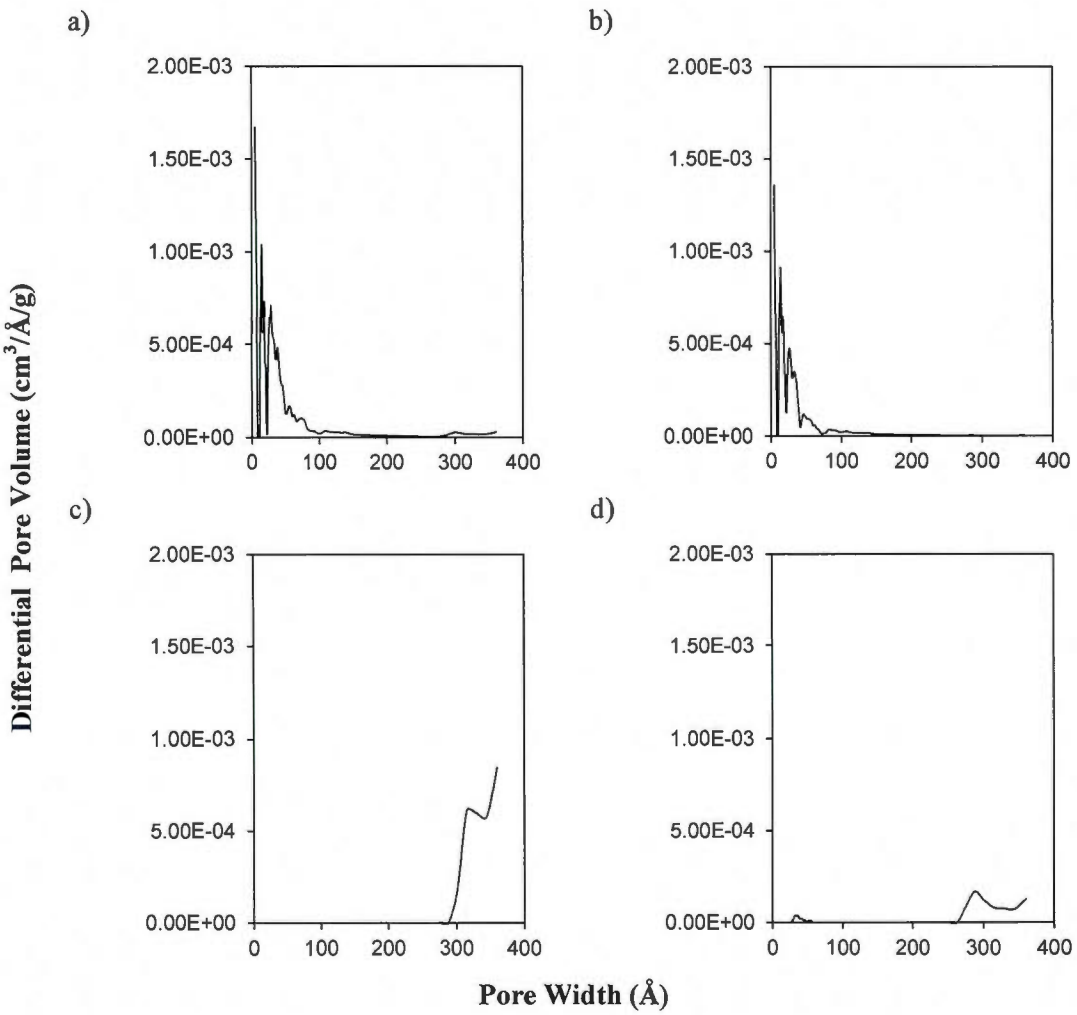



**Figure 2.4** Differential pore volume ($cm^3$/Å/g) versus pore widths (Å) for the recycled fibers from a) prepregs, b) Tooling, and virgin fibers from c) Torayca@ T700S and d) Panex® 35.

The surface chemistry of the carbon fibers was probed by XPS. Survey scans (Figure 2.5) showed carbon at a binding energy of 284.6 eV, followed by oxygen (532 eV), nitrogen (399 eV) and silicon (101 eV). Trace amounts of sodium (1070 eV), calcium (346 eV) and chlorine (198 eV) were also detected, and were most likely contaminants from the carbon fiber manufacturing process [7, 23].

Based on the survey scans, Table 2.4 displays the elemental composition on the surface of the carbon fibers. The oxygen to carbon ratio (O / C) is the most important parameter, as it

determines the concentration of oxygenated surface functional groups, which serve to improve wetting and interfacial adhesion with sizing and resin [14, 15]. However, a high O / C ratio (*i.e.* severe oxidation) forms fissures, causing a weak boundary layer that is detrimental to both interfacial adhesion, and the inherent mechanical properties of the fibers [15]. Epoxy sizing on the Toray fibers had a O / C ratio of 0.22 [7], while the O / C ratio for the recycled fibers from prepreg and tooling were 0.46 and 0.15 respectively. Pyrolysis processing heavily oxidized the surface of the prepreg fibers, which explains why it did not perform as well as the tooling fibers in micro-tensile testing. The Nitrogen content varied from 2 - 3 %, and was attributed to nitrogen containing functional groups present in PAN based precursors used during carbon fiber manufacturing, sizing, and residual resin. Tooling fibers were known to be contaminated with silicon; however, all the fibers contained significant amounts of it, suggesting that it must have been incorporated in sizing or resin.

In order to quantify the concentration of oxygenated surface functional groups, C 1s high resolution spectra (Figure 2.5) were curve fitted by 6 components according to a procedure described by Jiang *et al.* [7, 23]: a graphitic (C-C) peak at 284.6 eV, hydroxyl (C-OH) peak at 286.1 eV, carbonyl (C=O) peak at 287.6 eV, carboxyl (COOH) peak at 289.1 eV, carbonate ion ($CO_3^{2-}$) peak at 290.6 eV and $\pi$-$\pi^*$ transitions peak at 291.5 eV. The results are displayed in Table 2.5. The proportion of oxygenated surface functional groups did not change significantly; however, there was some evidence of surface oxidation by pyrolysis processing, as hydroxyl groups on the recycled fibers oxidized into higher oxidation state carbonyl groups. Both the recycled and Toray fibers showed evidence of carboxyl groups, making them favorable for wetting and adhesion with epoxy resin [28].

**Table 2.4** The surface elemental compositions (%) based on the XPS survey scans of the carbon fibers.

| Fiber Type | C 1s 285 eV | O 1s 532 eV | N 1s 399 eV | Si 2p 101 eV | Na 1s 1070 eV | Ca 2p 346 eV | Cl 2p 198 eV | O/C |
|---|---|---|---|---|---|---|---|---|
| Torayca@ T700S | 75.64 | 16.51 | 2.48 | 5.15 | 0.14 | 0.09 | - | 0.22 |
| Prepregs | 57.14 | 26.45 | 3.37 | 12.65 | - | - | - | 0.46 |
| Tooling | 82.56 | 12.44 | 2.81 | 1.87 | - | 0.17 | 0.14 | 0.15 |

**Table 2.5** Curve fitting results for the C 1s high resolution scans of the carbon fibers. Δ is the variation expressed in (%) with respect to Torayca@ T700S virgin carbon fibers.

| Fiber Type | C-C 284.6 eV | Δ | C-OH 286.1 eV | Δ | C=O 287.6 eV | Δ | COOH 289.1 eV | Δ | $CO_3^{2-}$ 290.6 eV | Δ | π-π* 291.5 eV | Δ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Torayca@ T700S | 61.84 | - | 24.24 | - | 2.87 | - | 8.85 | - | 0.00 | - | 2.20 | - |
| Prepregs | 63.73 | 1.89 | 19.82 | -4.42 | 6.61 | 3.74 | 6.78 | -2.07 | 0.83 | 0.83 | 2.22 | 0.02 |
| Tooling | 59.78 | -2.06 | 20.20 | -4.04 | 10.47 | 7.6 | 9.51 | 0.66 | 0.00 | 0 | 0.04 | -2.16 |

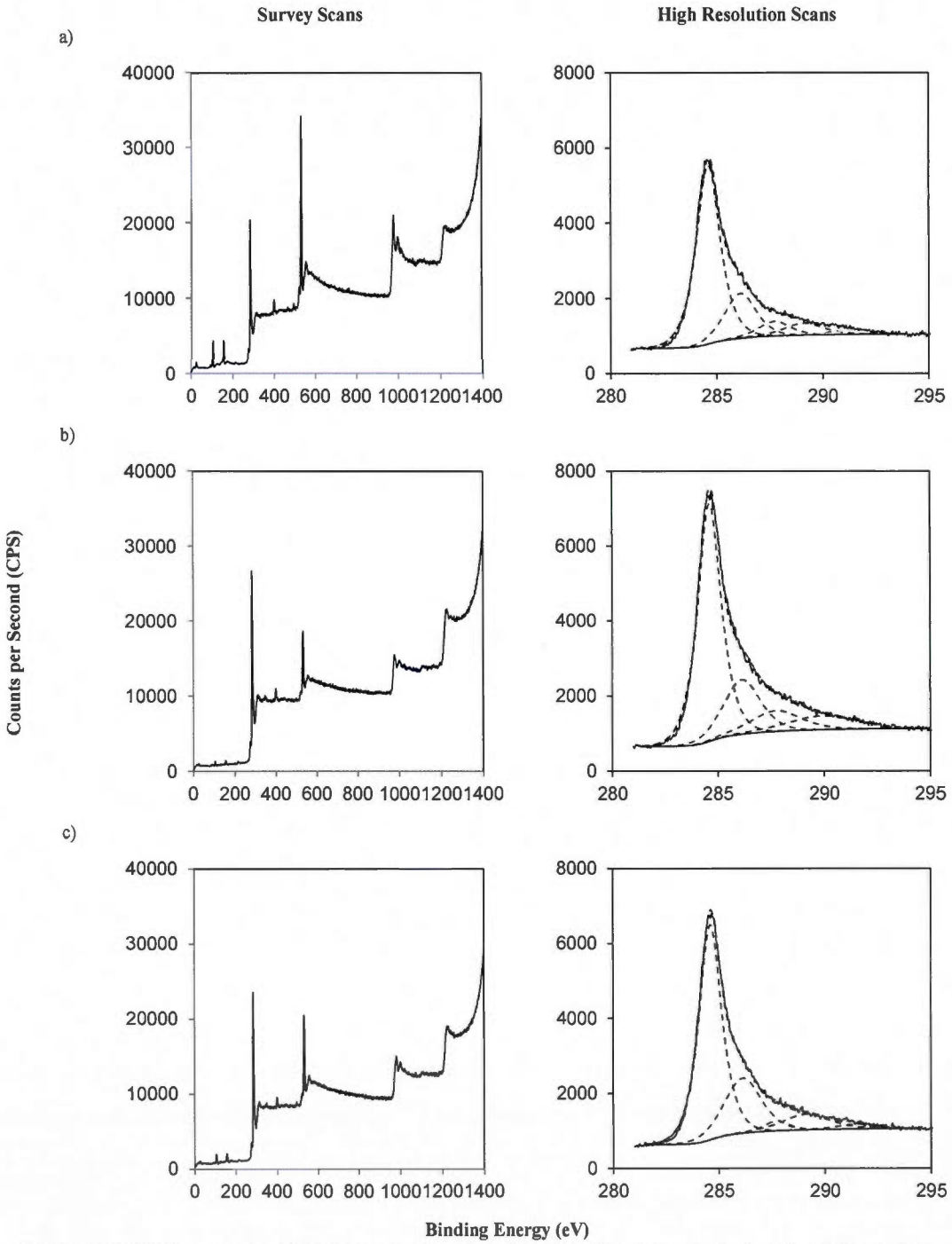



**Figure 2.5** XPS survey and high resolution C 1s spectra for the recycled carbon fibers from a) prepreg, b) tooling, and virgin carbon fibers from c) Torayca@ T700S.

Dynamic contact angle analysis (DCAA) probed the effect of pyrolysis processing on the wettability of the fibers by measuring their surface free energy at the macroscopic scale. According to the Van Oss-Chaudhury-Good method [14, 24], which utilizes contact angles, measured using liquid probes, the solid surface free energy term, $\gamma_s$ is related to contact angles as follows:

$$(\gamma_s^{LW}\gamma_l^{LW})^{0.5} + (\gamma_s^{+}\gamma_l^{-})^{0.5} + (\gamma_s^{-}\gamma_l^{+})^{0.5} = 0.5(1 + \cos\theta) \quad (2.3)$$

$$\gamma_s = \gamma_s^{LW} + \gamma_s^{AB} \quad (2.4)$$

$$\gamma_s^{AB} = 2(\gamma_s^{+}\gamma_s^{-})^{0.5} \quad (2.5)$$

where $\gamma_s^{LW}$ and $\gamma_l^{LW}$ are the Lifshitz - Van der Waal components, $\gamma_s^{+}$ and $\gamma_l^{+}$ are the electron acceptor components (i.e. lewis acid), and $\gamma_s^{-}$ and $\gamma_l^{-}$ are the electron donor components (i.e. lewis base) for the solid and liquid surfaces respectively. $\gamma_s^{AB}$ is the the lewis acid / base contribution of the solid surface, and is equal to the geometric mean between $\gamma_s^{+}$ and $\gamma_s^{-}$.

A system of 3 independent equations is required solve the 3 unknowns ($\gamma_s^{LW}$, $\gamma_s^{+}$, $\gamma_s^{-}$). Table 2.6 lists the 4 probe liquids that were used. n-hexane was used to determine the average fiber perimeter as it efficiently wets the surface (assume $\theta$ = 0 in equation 1). 1-bromonaphthalene is a non-polar liquid and is used to measure the Lifshitz - Van der Waal component, while water and glycerol are polar liquids and are used to measure the lewis acid / base components.

**Table 2.6** Surface free energy components (mN / m) of the probing liquids.

| **Liquid Probes** | $\gamma_l$ | $\gamma_l^{LW}$ | $\gamma_l^{+}$ | $\gamma_l^{-}$ |
|---|---|---|---|---|
| n-hexane [29] | 18.49 | 18.49 | - | - |
| 1-bromonaphthalene [30] | 44.4 | 44.4 | - | - |
| Water [15] | 72.8 | 21.8 | 25.5 | 25.5 |
| Glycerol [14] | 64 | 34 | 3.92 | 57.4 |

As shown in Table 2.7, the recycled fibers from prepreg and tooling had a surface free energy of 46±3 mN / m and 55.6±0.2 mN / m respectively, while the Toray fibers was

slightly lower at 45±1 mN / m because sizing covers up high energy sites [28]. The Lewis acid / base contribution compared to the total surface free energy of the fibers was significant, varying between 39 % to 54 % for the recycled fibers and 44 % for the Toray fibers. The Lewis acid / base contribution was attributed to the hydroxyl, carbonyl, carboxyl and carbonate oxygenated surface functional groups seen on the XPS C 1s high resolution scans, as they show strong Lewis acid / base behavior compared to graphene [14, 15]. Lewis acid / base interactions play an important role in carbon fiber / epoxy adhesion, as most notably, carboxyl groups can covalently bond with epoxy groups [28].

The surface of all fibers had an electron donor nature ($\gamma_s^- > \gamma_s^+$). For the Toray fibers, the electron donor nature of the surface was attributed to epoxy based sizing [14], while for the recycled fibers, it was attributed to the oxygenated surface functional groups and impurities. Pyrolysis processing altered the electron acceptor / donor balance, as hydroxyl groups oxidized into higher oxidation state carbonyl groups. Moreover, positively charged ions ($Na^+$, $Ca^{2+}$), as well as, residual resin and contaminants, also influenced the electron acceptor / donor nature of the oxygenated surface functional groups. Overall, the recycled fibers had high surface free energies with significant Lewis acid / base contributions, making them favorable for epoxy wetting and adhesion.

**Table 2.7** Surface free energy components (mN / m) of the carbon fibers.

| Carbon Fiber Type | $\gamma_s$ | $\gamma_s^{LW}$ | $\gamma_s^{AB}$ | $\gamma_s^+$ | $\gamma_s^-$ | $\gamma_s^{AB}/\gamma_s$ |
|---|---|---|---|---|---|---|
| Torayca@ T700S | 45±1 | 25±3 | 20±3 | 4±2 | 24±5 | 0.44 |
| Prepregs | 46±3 | 28±4 | 18±4 | 3±2 | 24±8 | 0.39 |
| Tooling | 55.6±0.2 | 25±3 | 30±3 | 8±1 | 27±2 | 0.54 |

Interfacial shear strength plays a critical role in stress transfer between fiber and resin in composite materials; additionally, it is a quantitative measure of interfacial adhesion [7, 14, 15, 23, 31]. Micro-droplet testing determined the interfacial shear strength of the carbon fibers with epoxy resin, and the results are displayed in Table 2.8. When compared to the Toray fibers, no difference was observed in the interfacial shear strength of the prepreg fibers, while, on average, tooling fibers had a 10 % lower value. The wettability study and

XPS results suggested that tooling fibers should have had a better adhesion than prepreg fibers because it had a higher surface free energy, Lewis acid / base contribution, and higher concentration of carboxyl groups, however, this was not the case. This contradiction can nonetheless be explained by the surface striations seen on the SEM micrographs of the prepreg fibers, which would have improved fiber / epoxy adhesion by mechanical keying [7, 23]. Despite the lack of sizing, the recycled fibers maintained their interfacial adhesion to epoxy resin.

**Table 2.8** Interfacial shear strength ($\tau$) of the carbon fibers. $\Delta$ is the variation expressed in (%) with respect to Torayca@ T700S virgin carbon fibers.

| Carbon Fiber Type | $\tau$ (MPa) | $\Delta$ (%) |
|---|---|---|
| Torayca@ T700S | 52±2 | - |
| Prepregs Fibers | 52±2 | 0 |
| Tooling Fibers | 47±2 | -10 |

## 2.6 Conclusion

Pyrolysis processing altered the surface properties of the recycled carbon fibers by effectively removing sizing and resin, thereby revealing surface topographies. Wetting and interfacial adhesion between the surface of recycled carbon fibers and epoxy resin were found to be predominantly affected by Lewis acid / base interactions of oxygenated surface functional groups, as well as, by mechanical interlocking. Mechanical interlocking appeared to be the more important parameter, as striated prepreg fibers out-performed the smooth tooling fibers in interfacial adhesion with epoxy resin despite their less attractive surface properties. Therefore, surface topographies are extremely important, and need to be assessed, when predicting the performance of re-manufactured composites containing recycled carbon fibers, as the interlaminar shear strength of composite structural materials correlates well with interfacial adhesion [14-16]. Finally, recycled carbon fibers have immense potential to be reintroduced as chopped fiber reinforcement in epoxy based composites, as they exhibited similar performance to virgin carbon fibers.

## 2.7 Acknowledgements

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CHAPITRE III

# CARDED RECYCLED CARBON FIBER MATS FOR THE PRODUCTION OF THERMOSET COMPOSITES VIA INFUSION / COMPRESSION MOLDING*

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## 3.1 Abstract

The use of carbon fiber reinforced thermoset composites has doubled in the last decade raising questions about the waste generated from manufacturing and at end-of-life, especially in the aircraft industry. In this study, 2.5 cm long carbon fibers were recovered from thermoset composite waste using a commercial scale pyrolysis process. Scanning electron microscopy, density measurements, single filament tensile testing as well as micro-droplet testing were performed to characterize the morphology, mechanical properties, and surface adhesion of the fibers. The recycled fibers appeared to be mostly undamaged and clean, exhibiting comparable mechanical properties to virgin carbon fibers. A carding process followed by an ultrasound treatment produced randomly aligned recycled fiber mats. These mats were used to fabricate composite plates, with fiber volume fractions up to 40 %, by infusion / compression molding. The mechanical properties of the plates were evaluated by tensile and flexural testing, and were found to be comparable to an equivalent containing virgin carbon fibers.

## 3.2 Introduction

In 2011, the global demand of carbon fiber tow rose to 45,800 tons. The aerospace industry accounted for 6,410 tons representing approximately 15 % of the carbon fiber market [1]. Carbon fibers are mainly used as reinforcement in polymeric matrices to create composite materials with higher strength to weight ratio and higher fatigue resistance than metals. In the past decade, the use of these carbon fibers reinforced plastics (CFRPs) increased significantly in aerospace with the development of the Boeing 787 Dreamliner and the Airbus A380 programs containing approximately 50 wt. % and 20 wt. % of CFRPs respectively [2]. This increase, however, has generated a significant amount of CFRP waste estimated at 3,000 tons per year in North America and Europe [3]. Currently, the vast majority of composite waste in North America is sent to landfills; therefore, aircraft manufacturers are under pressure to reduce waste through recycling or reuse, affecting both in-process waste and end-of-life disposal.

Environmental concerns have lead to strict management conditions with respect to composite waste especially in the European Union (EU). Since 2004, the Landfill Directive (1999/31/EC) [4] has rendered the disposal of composite waste to landfills illegal in many EU countries. Meanwhile, extended producer responsibility has set recycling targets for many types of waste. One important example is the end of life vehicle directive (2000/53/EC) [5], which states that after 2015; only 5 wt. % of an end-of-life vehicle can be sent to landfills. Therefore, recycling composite waste has been the subject of much investigation over the last 15 years. Yet, carbon fiber reinforced thermoset composites continue to be difficult to recycle [2, 6, 7], as they are a complex mixture of different materials such as thermosetting polymers, carbon fibers, and fillers; they may also contain foam cores, metal inserts, wire meshing, paints and other contaminants. Furthermore, the cross-linked nature of thermosetting polymers prevents remolding.

Several recycling technologies have been proposed and developed for CFRPs. They can be classified in two broad categories; mechanical grinding and fiber reclamation [2, 8]. Currently, fiber reclamation has gained momentum because of its ability to recover high

quality carbon fibers by employing either a chemical or thermal process to break down thermosetting resin. Fiber reclamation is particularly suitable for CFRPs due to the high chemical and thermal stability of carbon fibers [2, 8]. The most common fiber reclamation process is pyrolysis [2, 8, 9]. It is defined as the thermal degradation (400 - 700 °C) of organic material (i.e. polymeric matrix) in an inert environment (usually CO, $CO_2$, or $N_2$). Other fiber reclamation technologies include catalytic conversion [8, 10, 11], fluidized bed reactor [2, 8, 12, 13] and supercritical fluids [14, 15].

In addition to the legislative "push" factor, another driving force for developing fiber reclamation technologies is the savings in terms of energy of production. Manufacturing virgin carbon fibers requires a tremendous amount of energy estimated at 55 kWh / kg to 165 kWh / kg [2]. Recovering carbon fibers from CFRPs, on the other hand, requires only around 3 kWh / kg to 10 kWh / kg [2]. Therefore, economic viability of recycling CFRPs can be achieved if applications can be found for recycled carbon fibers. To this end, the feasibility of using carded recycled carbon fiber mats and epoxy resin to fabricate thermoset composite plates by infusion / compression molding was investigated in this study.

## 3.3 Materials

### 3.3.1 Carbon Fibers

Carbon fibers were recovered from a 100 kg sample of carbon fiber reinforced thermoset composite waste generously donated by Bell Helicopter Textron Canada Ltd (BHTCL: Mirabel, Quebec, Canada). This sample represents an actual sample of the waste composition generated by the Canadian aerospace industry. It contained carbon fiber prepregs (cured and uncured) based on epoxy and bismaleimide resins, and tooling parts made from carbon fiber reinforced epoxy with trace amounts of silicone. Pyrolysis was performed at Materials Innovation Technologies (MIT: Lake City, South Carolina, United States) using their commercial scale batch pyrolysis oven. Before pyrolysis, the waste was sorted and cut into 2.5 cm x 2.5 cm fragments to limit the fiber length distribution, thereby controlling the overall uniformity of the recycled fibers. Pyrolysis was performed at low temperatures (< 400 °C) under a controlled atmosphere, and the residence time was adjusted

as a function of the material to be pyrolyzed. Recycled carbon fibers were obtained from prepregs and tooling. Toray T700SC (sized, tensile modulus: 230 GPa, tensile strength: 4,900 MPa) virgin carbon fibers were chosen as a reference material, and cut into lengths of 2.5 cm.

### 3.3.2 Resin

PRISM™ EP2400, produced by Cytec Engineered Materials, is an infusion grade epoxy used to fabricate the carbon fibers / epoxy plates, with processing properties as listed in Table 3.1.

**Table 3.1** Properties of the infusion grade epoxy PRISM™ EP2400 produced by Cytec Engineered Materials.

| **Properties** | **PRISM™ EP2400** |
|---|---|
| Injectable Temperature (°C) | 70 |
| Cure Temperature (°C) | 180 |
| Dry $T_g$ (room temperature, dry) | 179 |
| Wet $T_g$ (48 hour water boil, wet) | 163 |
| Toughness | Very High |
| Cured Resin Density (g/cm$^3$) | 1.24 |

## 3.4 Experimental

### 3.4.1 Characterization of the Carbon Fibers

Fiber surface morphology was probed using a Jeol GSM 6100 scanning electron microscope (SEM) operating at 10 kV. Fiber diameters were measured using ImageJ software [16]. Reported values are the average of 5 samples for each fiber type. The prepreg fiber density was measured using a gas pycnometer (Humipyc from InstruQuest, gas: helium, measurement pressure: 210 kPa ± 3 Pa, stabilization time: 300 s, temperature: 21.5 ° C, relative humidity: 17 %). Reported values are the average of 3 measurements. Micro-tensile testing was performed on mono-filaments according to ASTM D3379 [17] using an Instron Microtester equipped with a 2N load cell. A gage length of 10 mm and rate of 1 mm / min were used. Reported values are the average of 30 samples for each fiber type. In all cases, error bounds represent the 95 % confidence limits for a student-t distribution.

### 3.4.2 Characterization of the carbon fibers / epoxy adhesion

Micro-droplet testing [12, 18, 19] was used to quantify the interfacial shear strength ($\tau$), i.e. the adhesion between the fiber and epoxy matrix. A normal force was applied on a micro-droplet of resin using shearing blades that pull the resin off the fiber. Assuming a cylindrical model, the interfacial shear strength is calculated by:

$$\tau = F/\pi D_f L \tag{3.1}$$

where $F$ is the debonding force, $D_f$ is the fiber diameter, and $L$ is the embedded length.

Samples were prepared by gluing the ends of carbon mono-filaments onto 4 cm x 1 cm paper templates with a punch hole through the middle. Elliptical epoxy droplets were applied onto the monofilaments using a fine metal applicator connected to a heated soldering iron. Samples were cured in an oven for 2 hours at 180 °C. Droplets with embedded lengths varying between 20 μm to 50 μm were chosen for testing. Observations were made using a Nikon Eclipse 50i optical microscope connected to a QImaging Go-3 camera, and measurements were made using ImageJ software calibrated with a Pyser-SGI S8 stage micrometer graticule. A caliper attached to a Micos MT-65 linear stage served as shearing blades. The caliper opening was set to 10 μm and the speed was set to 0.1 mm / min. Force measurements were acquired using a Mettler Tolledo AB135-s/FACT balance connected to a computer using LabView software. Reported values are based on 15 observations for each fiber type.

### 3.4.3 Carbon fibers / epoxy composite plates fabrication

Recycled carbon fibers were transformed from a "fluffy" material to a mat by the following procedure. A roto-carder separated, interlocked and partly aligned the fibers. To remove surface impurities and debris, the fibers were placed on a 25 cm x 31 cm frame, subjected to ultrasonic treatment for 5 minutes, and washed with distilled water. The resulting mats were dried in an oven at 115 °C for 24 h to remove residual water. Upon visual inspection, fibers appeared to be evenly distributed throughout each mat. The mats had a

mass of approximately 19 g. A similar method was used to prepare mats containing virgin carbon fibers.

As shown in Figure 3.1, carbon fibers / epoxy plates were fabricated by a combination of infusion / compression moulding. Mats were laid on an aluminium tool, and a peel ply and flow distribution media were placed over them. A vacuum bag was used as formable matched mold. After degassing, epoxy was injected at 80 °C via a heated injection line, and vacuum was applied at the end of the plates. Once entirely impregnated with epoxy, plates were placed in a heated press for 2 hours at 180 °C, and compressed to 3 mm with a pressure of 60 tons.

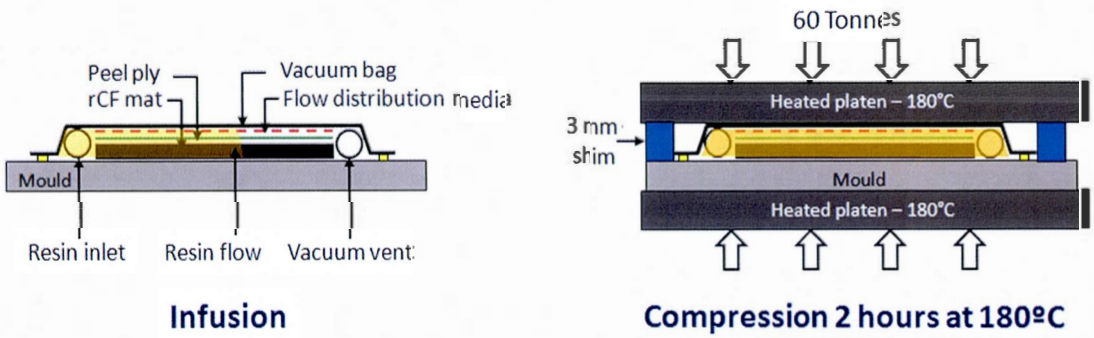


**Figure 3.1** Schematic representation of the infusion / compression moulding process.

### 3.4.4 Characterization of the carbon fibers / epoxy composite plates

Test specimens were cut from the plates by water jet saw (Figure 3.2). Density specimens were collected at positions A, B, C and D, and porosity specimens were collected at positions A', B' and C'. Tensile and flexural specimens measured 25 mm x 250 mm x 3 mm and 12.5 mm x 64 mm x 3 mm respectively.

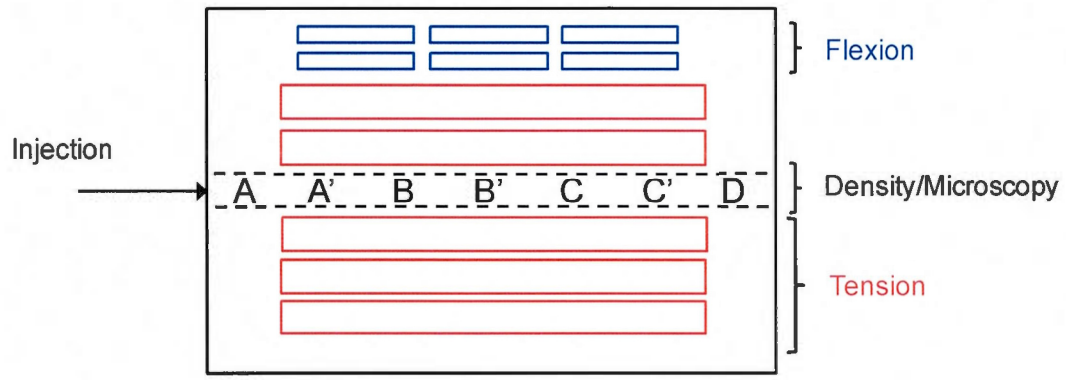


**Figure 3.2** Geometry and position of the test specimens cut from the carbon fibers / epoxy plates.

*Fiber volume fraction.* The fiber volume content ($v_f$) was controlled by the mass of fibers used per plate (number of mats per plate), and is calculated by:

$$v_f = \frac{m_f/\rho_f}{m_f/\rho_f + m_m/\rho_m} \tag{3.2}$$

where $m_f$ is the mass of fibers, $\rho_f$ is the fiber density (as measured for the recycled fibers and 1.80 g / cm$^3$ for the virgin fibers), $m_m$ is the mass of epoxy and $\rho_m$ is the epoxy density (1.24 g / cm$^3$ for PRISM$^{TM}$ EP2400).

*Density.* The experimental plate density ($\rho_{,c,1}$) was measured by weighing samples in water and air, and is calculated by:

$$\rho_{c,1} = \frac{m_{c,air}}{m_{c,air} - m_{c,water}} * \rho_{H_20} \tag{3.3}$$

where $m_{c,air}$ and $m_{c,water}$ are the specimen masses in air and in water respectively, and $\rho_{H_20}$ is the water density (0.9977 g / cm$^3$ at 22.5 °C [20]).

Based on the experimental fiber volume fraction determined in equation 3, the theoretical plate density ($\rho_{c,2}$) is calculated by:

$$\rho_{c,2} = v_f \rho_f + (1 - v_f)\rho_m \tag{3.4}$$

*Porosity*. Polished cross-sections of recycled carbon fibers / epoxy plates were probed by SEM in order to confirm the presence of porosities, and to examine the distribution of fibers within the material.

*Mechanical Properties*. The plates were tested under uniaxial tension according to ASTM D3039 [21] using an Instron 5582 equipped with a 100 kN cell; the applied crosshead speed was 2 mm / min. Flexion tests (3-point bending) were performed according to ASTM D790 [22] using an Instron 1123 equipped with a 5 kN cell; the applied crosshead speed was 1.3 mm / min with a span of 48 mm. Reported tensile and flexural values are the average of 5 measurements for each plate.

## 3.5 Results & Discussion

### 3.5.1 Characterization of the Carbon Fibers

SEM micrographs (Figure 3.3) show that the prepreg and tooling fibers were generally clean and appeared relatively undamaged having no obvious cracks. Their diameters measured 6.5 ± 0.8 μm and 6.5 ± 0.9 μm respectively. Prepreg fibers exhibited surface striations designed to improve their adhesion with epoxy, and residual resin was often observed, probably due to a lack of optimization of the pyrolysis process (the process was optimized for epoxy composites, whereas the prepreg waste contained both epoxy and bismaleimide resins). The tooling fibers showed some loose debris and no surface striation. The average density of the prepreg fibers was determined by pycnometry to be 1.75 g / $cm^3$, close to value of the Toray fibers (1.80 g / $cm^3$).

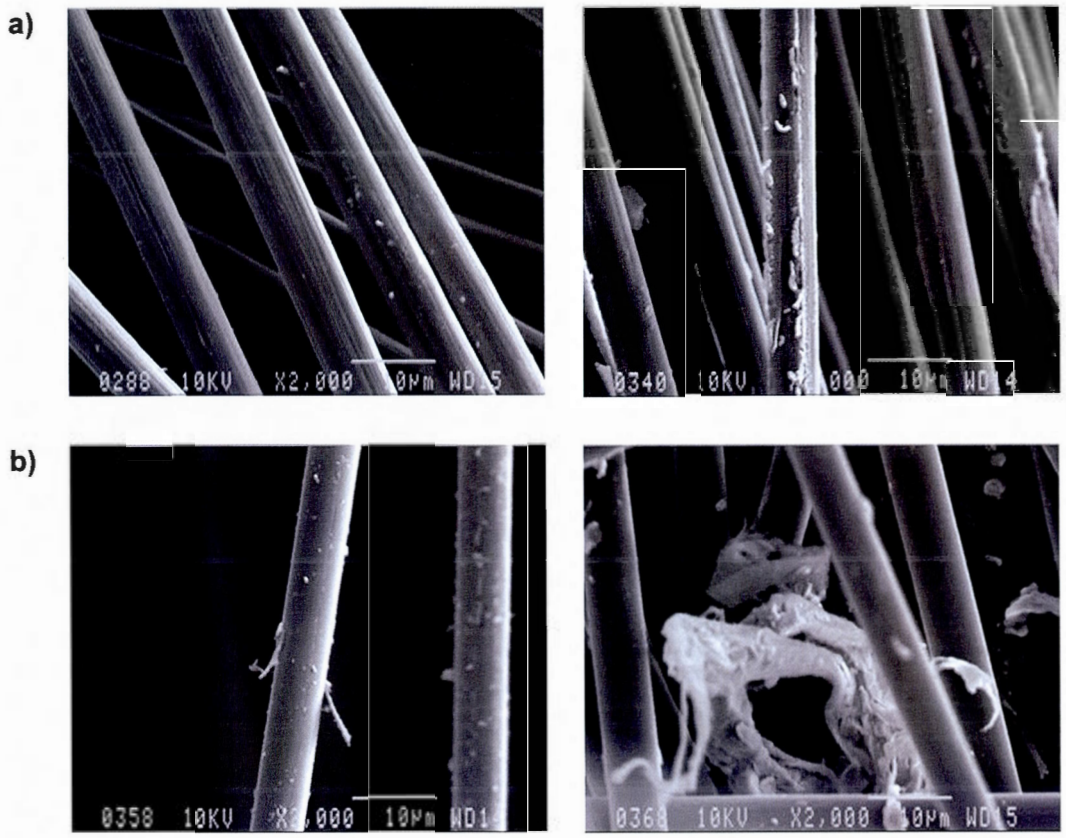


**Figure 3.3** SEM micrographs of the recycled carbon fibers from a) prepregs, b) tooling

The recycled fibers from prepregs and tooling had a tensile modulus of 160 ± 20 GPa and 170 ± 10 GPa, and a maximum tensile strength of 3400 ± 400 MPa and 3800 ± 200 MPa, respectively (Figure 3.4). When compared to the virgin fibers, average differences of around -10 % to - 5 % in tensile modulus and - 22 % to - 13 % in maximum tensile strength were observed. Tooling fibers offered a better mechanical performance than prepreg fibers, although prepregs contain high performance aerospace grades of carbon fibers, while tooling composites generally contain industrial grades of carbon fibers. This result may be due to process variations that can occur during recycling. Therefore, further optimization of the pyrolysis conditions (temperature, residence time, and atmosphere), with respect to the type of composite waste being treated, should contribute to further improving the properties of the fibers. Overall, the recycled fibers retained most of their mechanical properties.

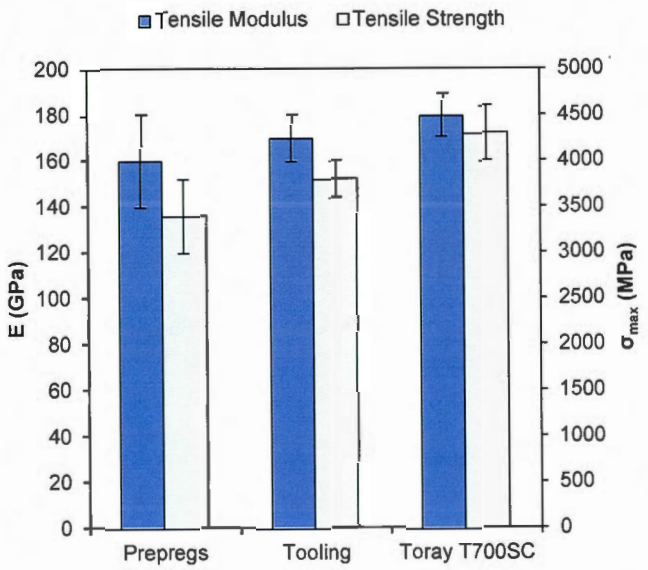


**Figure 3.4** Tensile modulus E (GPa) and maximum tensile strength $\sigma_{max}$ (MPa) of the recycled carbon fibers from prepregs and tooling, and virgin carbon fibers from Toray T700SC.

### 3.5.2 Characterization of the carbon fiber / epoxy adhesion

Figure 3.5 plots the force at debonding versus embedded length of the microdroplet data. Regression analysis produced a linear trend for each fiber type; thus, the interfacial shear strength was calculated from:

$$\tau = \beta/\pi D_f \tag{3.5}$$

where $\beta$ is the slope of the $F$ vs. $L$ regression curve, $D_f$ is the fiber diameter (6.5 μm recycled fibers, 7 μm virgin fibers).

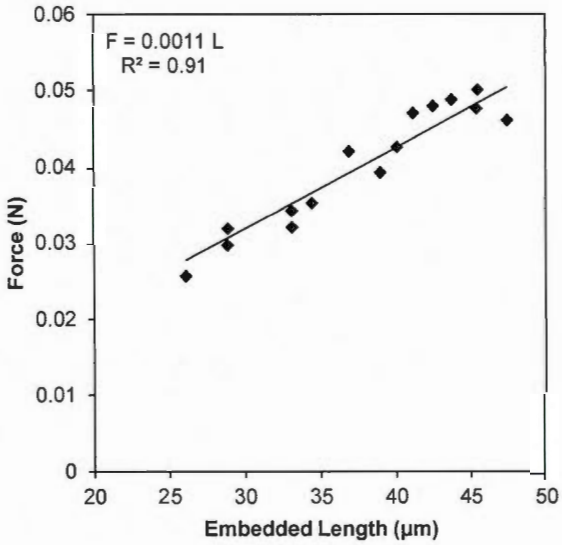


**Figure 3.5** Force (N) versus Embedded Length (μm) of the recycled carbon fibers from prepregs for the microdroplet test.

When compared to the virgin fibers (Table 3.2), no difference was observed in the interfacial shear strength values for prepreg fibers, while, on average, tooling fibers have a 10 % lower value. This difference may be explained by the surface striations seen on the SEM micrographs of the prepreg fibers, which could improve fiber / matrix adhesion. Despite the lack of sizing, the recycled fibers maintain their interfacial properties.

**Table 3.2** Interfacial shear strength ($\tau$) of the recycled carbon fibers from prepregs and tooling, and virgin carbon fibers from Toray T700SC. $\Delta$ is the variation expressed in % with respect to the Toray fibers.

| Carbon Fiber type | $\tau$ (MPa) | $\Delta$ (%) |
|---|---|---|
| Toray T700SC | 52±2 | - |
| Prepregs Fibers | 52±2 | 0 |
| Tooling Fibers | 47±2 | -10 |

### 3.5.3 Characterization of the carbon fiber reinforced epoxy composite plates

Table 3.3 lists the carbon fibers / epoxy plates fabricated by infusion / compression moulding. Three plates with prepreg fibers, three plates with tooling fibers, and two plates with virgin fibers were fabricated. Plates T1 and NR4 were not mechanically tested. The fiber volume fraction ($v_f$) varied from 23 % to 40 %.

**Table 3.3** A List of the carbon fibers / epoxy composite plates produced by infusion / compression moulding.

| Material | Sample | $v_f$ (%) | $w_f$ (%) |
|---|---|---|---|
| Epoxy / Prepreg Fibers | P1 | 38 | 47 |
| | P2 | 36 | 44 |
| | P3 | 40 | 50 |
| Epoxy / Tooling fibers | T1 | 23 | 30 |
| | T2 | 28 | 35 |
| | T3 | 34 | 42 |
| Epoxy / Toray T700SC | NR3 | 40 | 50 |
| | NR4 | 38 | 47 |

Figure 3.6 displays the composite density along the injection direction of each plate. Variations in density are likely due to the presence of porosities in the plates as well as a difference in fiber distribution from one position to another. The presence of porosities was confirmed by SEM micrographs of plates P3 and T3 (Figure 3.7); voids seemed to be evenly distributed throughout P3, while in T3, they are mainly observed at the outlet position C'.

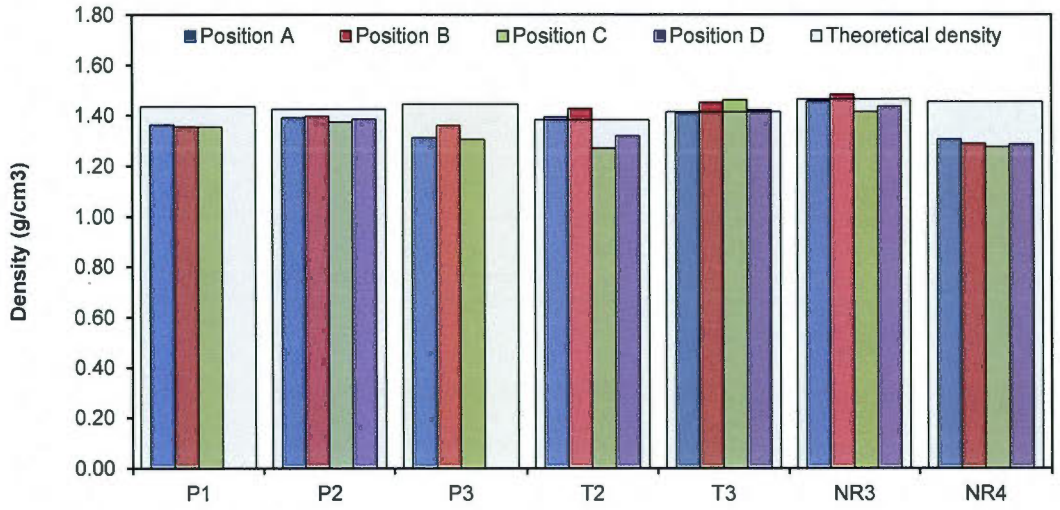


**Figure 3.6** Variation of composite density along the injection direction for the carbon fibers / epoxy plates.

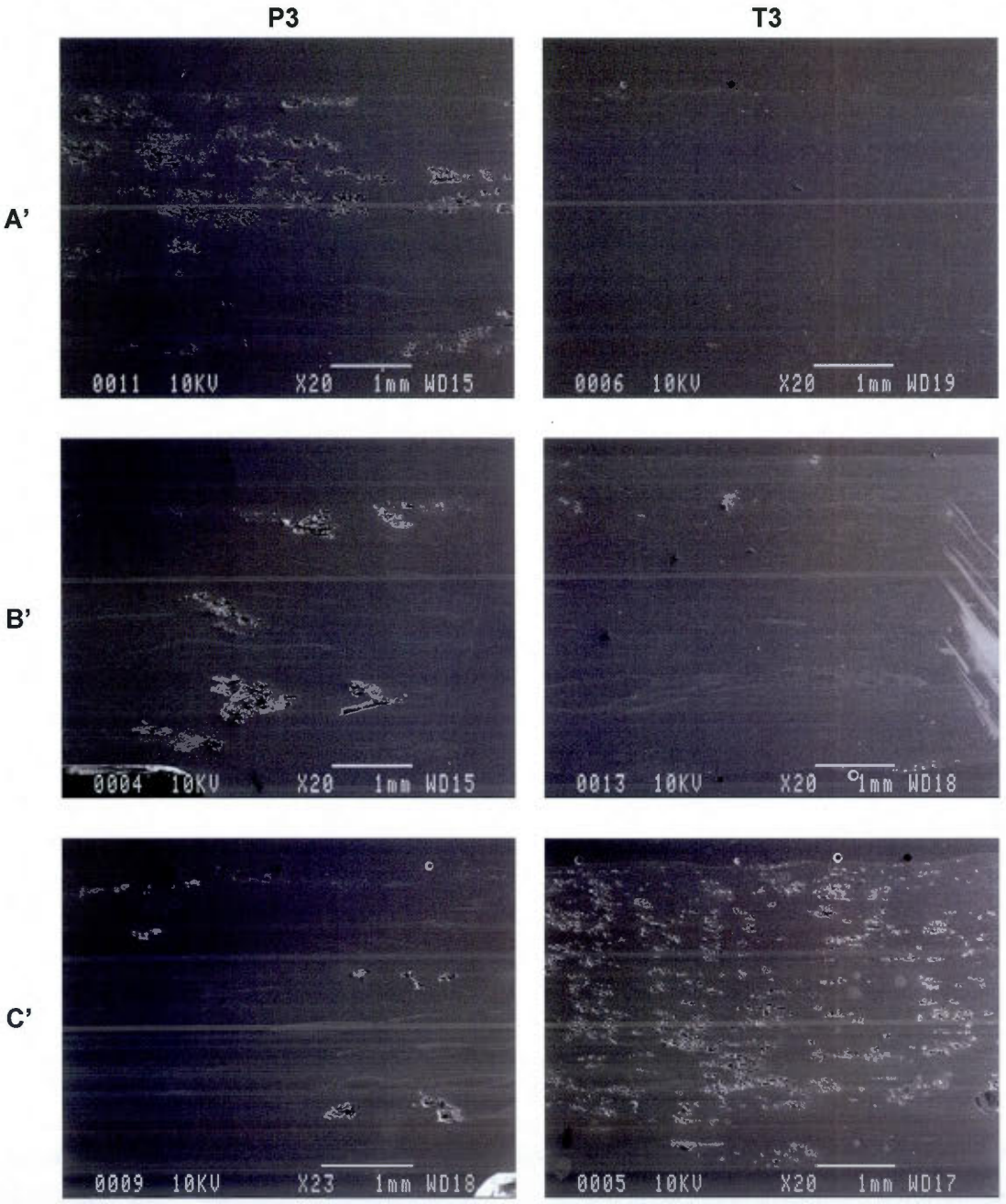


**Figure 3.7** SEM micrographs of the polished cross-sections along the injection direction of plates P3 and T3.

Tensile (Figure 3.8 and Figure 3.9) and flexural testing (Figure 3.10) showed, as expected, higher fiber volume fractions lead to better mechanical properties. The addition of recycled fibers in the plates increased the tensile and flexural modulus, on average, by a factor of at least 6, while the maximum tensile strength and flexural strength at yield increased by a factor of at least 2 when compared with pure epoxy. These results confirm that the recycled fibers act as reinforcement, and not as simple filler. For the same volume fraction, the virgin fibers / epoxy plate (NR3) exhibited slightly better mechanical properties than the plates containing recycled fibers. This difference is attributable to; the inherent mechanical performance of the carbon fibers, the overall fiber and void distributions within the plates, as well as the fiber / matrix adhesion (presence of sizing on the virgin fibers). Therefore, the quality and performance of the plates containing recycled fibers should be improved by increased control over the fiber volume fraction (via composite thickness) and void content, increased homogeneity of the recycled fiber mats, and incorporating an epoxy compatible sizing at the surface of the recycled fibers.

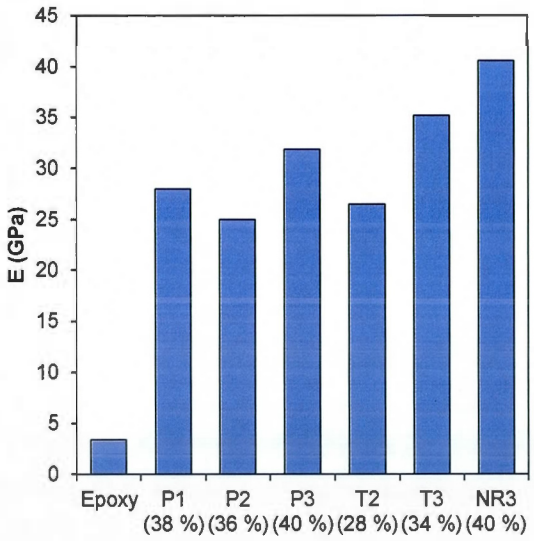


**Figure 3.8** Tensile modulus E (GPa) of the carbon fibers / epoxy plates.

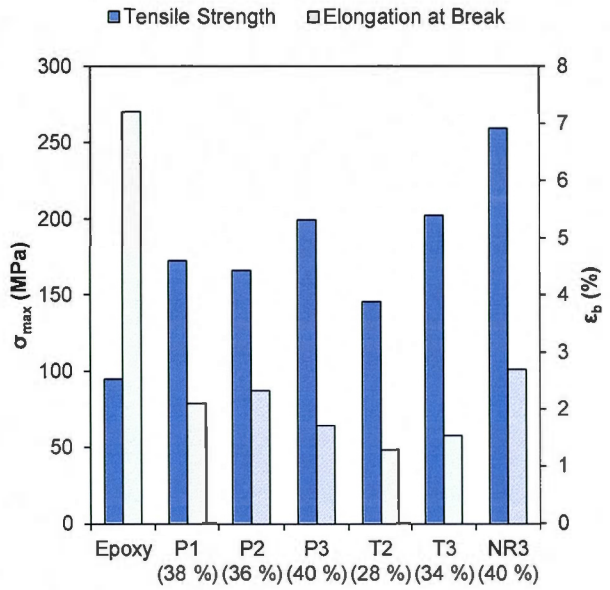


**Figure 3.9** Maximum tensile strength $\sigma_{max}$ (MPa) and elongation at break $\varepsilon_b$ (%) of the carbon fibers / epoxy plates.

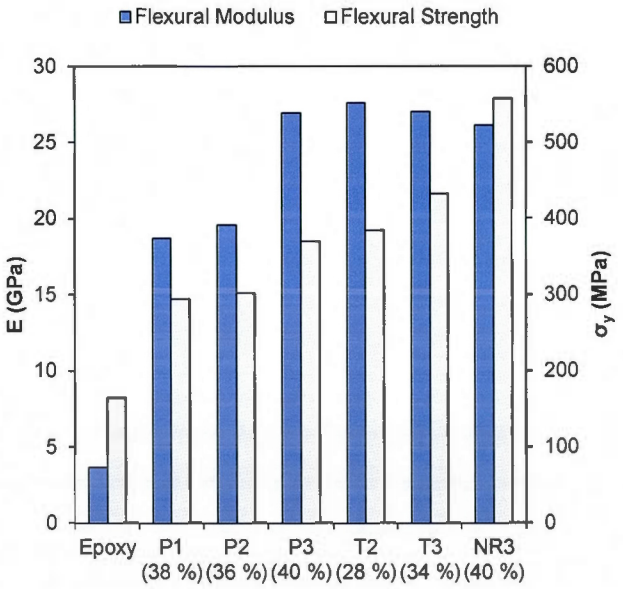


**Figure 3.10** Flexural modulus E (MPa) and flexural strength at yield $\sigma_y$ (MPa) of the carbon fibers / epoxy plates.

## 3.6 Conclusion

In this study, carbon fibers were recovered from carbon fiber reinforced thermoset composite waste generated by the aircraft industry using Materials Innovation Technologies commercial scale pyrolysis process. Electron microscopy, density measurements, mono-filament tensile testing and micro-droplet testing determined that the recycled carbon fibers retain most of their mechanical and surface adhesion properties. The feasibility of fabricating recycled carbon fiber reinforced thermoset composites was also demonstrated. A carding process produced homogeneous recycled fiber mats that were subsequently manufactured into composite plates by infusion / compression moulding with epoxy. Fiber volume fractions up to 40% were obtained. Tensile and flexural testing determined that plates containing recycled fibers exhibited better mechanical properties than pure epoxy, and similar properties to a plate containing virgin fibers, despite the presence of porosities. This demonstrates the potential of reintegrating recycled carbon fibers as reinforcement in new thermoset composites for a variety of applications.

## 3.7 Acknowledgements

This project (identified as CRIAQ ENV-411 project) was supported by the Consortium for Research and Innovation in Aerospace in Quebec (CRIAQ), Bell Helicopter Textron Canada Ltd (Mirabel, Quebec, Canada) and Bombardier Aerospace (Montreal, Quebec, Canada). The authors would like to thank Karen Stoeffler, Fréderic Busnel, and Éric Patenaude from the National Research Council of Canada for their advice and help on the manufacturing of composite plates.

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# CHAPITRE IV

# CONCLUSION

In this work, chopped recycled carbon fibers from prepreg and tooling were recovered from carbon fiber reinforced thermoset composite waste generated by the Canadian aircraft industry, using Materials Innovation Technologies commercial scale pyrolysis process. Pyrolysis processing altered the surface properties of the recycled carbon fibers by effectively removing sizing and resin, thereby revealing surface topographies. The mechanical performance of the recycled fibers were comparable to that of the virgin fibers, with a decrease in tensile modulus of < 10 %, a decrease in tensile strength of < 22 %, and a decrease in interfacial adhesion to epoxy resin of < 10 %.

This work demonstrated that recycled carbon fibers can be reintegrated in thermosetting resin producing high quality composites. The epoxy / recycled carbon fiber plates, fabricated by infusion / compression molding of carded recycled carbon fiber mats, had a comparable mechanical performance to a virgin equivalent with a decrease in tensile modulus and strength of < 10 %; however, several recommendations can be made to optimize the quality and performance of the fabricated composites, as well as, the molding process:

- The quality of the mats has to be improved to reach a more homogeneous distribution of the recycled carbon fibers. Moreover, preferential alignment of the fibers can improve anisotropic properties of the fabricated composites.

- The infusion / compression molding process needs to be optimized to better control the fiber volume fraction and void content.

- The incorporation of an epoxy compatible sizing at the surface of the recycled carbon fibers should be investigated to enhance adhesion at the fiber / epoxy resin interface.

Moreover, surface topographies of the recycled carbon fibers need to be assessed prior to molding, as they have a significant effect on interfacial adhesion with epoxy resin.

- Scaling-up of fabrication process. This includes cleaning and preparation of the recycled carbon fiber mats, as well as, molding of the final composite piece.

In addition, Sheet Molding Compounding (SMC) should be investigated as an alternative method for manufacturing epoxy / recycled carbon fiber composites, since this fabrication method allows for the incorporation of higher fiber contents, and leads to a better consolidation of the material.

Finally, this thesis confirms the huge potential of re-manufacturing high quality thermoset composites from recycled carbon fibers. Such materials might be suitable for applications in the aerospace industry or in other markets.

# APPENDIX A

## SUMMARY

During my master's, I had an internship from August 2011 until February 2012 at the National Research Council Canada (NRC), under the supervision of my co-sponsors Nathalie Legros and Karen Stoeffler. I worked on a project identified as CRIAQ ENV-411, which was supported by the Consortium for Research and Innovation in Aerospace in Quebec (CRIAQ), Bell Helicopter Textron Canada Ltd. (Mirabel, Quebec, Canada) and Bombardier Aerospace (Montreal, Quebec, Canada). This project resulted in the following work:

- A report entitled "Recycling of Thermoset Composites Wastes from Aerospace Industry: Feasibility Study and Proof of Concept" was produced, and is currently under a confidentiality agreement. The portion discussing composite waste legislation is presented in Section A.1 of the appendix. In addition, it was presented as a poster at a CRIAQ conference.

  - Stoeffler K, Khoun L, Legros N, **Andjelic S**, Schougaard SB, Roberge J, Chowdhury S, Corrigan J, Dezombre J, Iordan A, Oudiehani K. Recycling of Thermoset Composite Wastes From Aerospace Industry: Feasibility Study and Proof of Concept. 10th Anniversary Gala CRIAQ. 2012. Montreal, Quebec, Canada.

- A scientific article entitled "Effect of Morphological, Mechanical and Surface Properties on the Wettability and Interfacial Adhesion of Recycled Carbon Fibers" is intended for publication in the Journal of Material Science, and is reproduced in Chapter II.

- A technical paper entitled "Carded Recycled Carbon Fiber Mats for the Production of Thermoset Composites via Infusion / Compression Molding" was accepted and published in SAE International, and is reproduced in Chapter III. This manuscript was presented as an oral presentation at the SAE 2013 AeroTech Congress & Exhibition, held on September 24-26, 2013 at Palais des congrès, in Montreal, Quebec, Canada.

- **Andjelic S**, Khoun L, Legros N, Roberge J, Schougaard SB. Carded Recycled Carbon Fiber Mats for the Production of Thermoset Composites via Infusion / Compression Molding. SAE International. 2013.

- A scientific article entitled "Polyphenylene sulfide (PPS) composites reinforced with recycled carbon fiber" was accepted and published in Composites Science and Technology. A copy of the article is reproduced in Section A.2 of the appendix.

- Stoeffler K, **Andjelic S**, Legros N, Roberge J, Schougaard SB. Polyphenylene sulfide (PPS) composites reinforced with recycled carbon fiber. Composites Science and Technology. 2013; 84(0): 65-71.

Section A.1 covers legislation on composite waste disposal, while Section A.2 presents the published article mentioned above.

# A.1 Composite Waste Legislation

## 2. Thermoset composites recycling

### 2.1. Government Regulations

#### 2.1.1. Introduction

Governments are currently setting up legislation in order to decrease the amount of waste that is produced, discarded, and disposed of. While methods may vary, the goals of waste management are always the same: promoting the waste management hierarchy (reduce, reuse, recycle, recover and disposal) and reducing the amount of waste that is sent to landfills. This section will examine current and upcoming legislation concerning waste management in Canada and Europe. The main focus will be on the management of thermoset composite waste.

#### 2.1.2. Waste Management in Canada

##### *2.1.2.1. Overview*

In Canada, the responsibility of managing waste is shared amongst the federal, provincial / territorial, and regional / municipal governments. The federal government is responsible for managing the international and interprovincial movement of hazardous waste destined for recycling or disposal. The provincial / territorial governments have jurisdiction over the transportation of hazardous waste within its boundaries, as well as the licensing and permitting of authorized facilities undertaking the reclamation, recycling, or disposal of waste[1].

##### *2.1.2.2. Management of End-of-Life Products in Canada*

Approximately 1.2 million vehicles are taken off the road every year in Canada. This amounts to nearly 150 000 t / year of vehicle waste that ends up in landfills[2]. Given that the volume of waste produced by the automobile industry far outweighs that produced by the aerospace industry; it is safe to assume that any legislation concerning End-of-Life (EOL) vehicles will be a precursor for EOL aircraft legislation. Canada has lagged behind many countries in the world in addressing this issue and there are nearly no laws in place dealing with EOL vehicles[2,3].

The management of other EOL products is governed by both Extended Producer Responsibility (EPR) and Product Stewardship programs[4]. An EPR program specifically identifies end-of-life management of products as the responsibility of producers (e.g. brand owners, first importers or manufacturers), whereas a Product Stewardship program allocates the responsibility to

provincial / territorial or regional / municipal governments. The main difference between the two approaches is that funding for EPR programs is provided by the producers. Therefore, if an EPR program were developed for EOL aircrafts, it would put the responsibility of managing such waste on aircraft manufacturers.

#### *2.1.2.3. Waste Management in Quebec*

a) Overview

In 2008, 13 million tonnes of waste was generated in Quebec amounting to 1.69 t / capita. 52% of this waste was treated, leaving 810 kg / capita of waste that was disposed of. Therefore, there is an undeniable potential in further developing reclamation and recycling technologies. To demonstrate this key point, in 2006, 2.5 million tons of the most commonly recycled residual materials that were recovered generated $ 550 million and created over 10 000 jobs[5].

In Quebec, waste (a.k.a. residual materials) management is governed by the Environmental Quality Act (EQA, 1999)[6] and enforced by the Minister of Sustainable Development, Environment and Parks. There is no specific regulation for the management of composite waste; thus, they are treated on a case by case basis, by applying the EQA (sections 20, 22, and 66, Table 1) and by examining the regulations on residual materials (Regulation Respecting Solid Wastes, Regulation Respecting the Landfilling and Incineration of Residual Materials, Regulation Respecting the Charges Payable for the Disposal of Residual Materials) and the regulations on hazardous residual materials (Regulation on Hazardous Materials).

*Table 1. Description of the sections 20, 22 and 66 of the Environmental Quality Act[6].*

| Section | Environmental Quality Act |
|---|---|
| 20 | No one may emit, deposit, issue or discharge or allow the emission, deposit, issuance or discharge into the environment of a contaminant in a greater quantity or concentration than that provided for by regulation of the Government. |
| 22 | No one may erect or alter a structure, undertake to operate an industry, carry on an activity or use an industrial process or increase the production of any goods or services if it seems likely that this will result in an emission, deposit, issuance or discharge of contaminants into the environment or a change in the quality of the environment, unless he first obtains from the Minister a certificate of authorization. |
| 66 | No one may deposit or discharge residual materials or allow residual materials to be deposited or discharged at a place other than a site at which the storage, treatment or elimination of residual materials is authorized by the Minister or the Government pursuant to the provisions of this Act and the regulations. |

b) The Residual Materials Management Policy

The Quebec Residual Materials Management Policy[5] provides insight into the future of residual materials management in Quebec. This policy reflects the government's intent to build a green economy and is accompanied by a 5 year Action Plan. Its main goals are to create a zero-waste society and to dispose of only end-waste. It includes measures (regulations, programs, amendments, reports, etc.) that will address the three main challenges of residual materials management:

- Ending resource waste
- Promoting the goals and achievements of the Climate Change Action Plan and of the Quebec Energy Strategy
- Making all stakeholders involved responsible for residual materials management.

The quantitative goals of the Action Plan are the following:

- By the end of 2015, the amount of residual materials sent for disposal must decrease from 810 kg / capita to 700 kg / capita
- 70% of paper, cardboard, plastic, glass and metal waste must be recycled
- 60% of organic putrescible waste must be processed
- 80% of concrete, brick, and asphalt waste must be either recycled or reclaimed
- 70% of construction, renovation, and demolition waste from the building segment must be sorted at the source or sent to a sorting center.

To reach these goals, 10 intervention strategies have been set up:

1. Maintain the 4R-D hierarchy (reduce, reuse, recycle, recover and disposal)
2. Prevent and reduce the production of residual materials
3. Discourage and monitor disposal
4. Ban the disposal of organic material
5. Make producers more responsible
6. Support regional planning and performance
7. Stimulate the performance of the industrial and construction sectors
8. Choose the most efficient collection system
9. Know, inform, raise awareness, and educate
10. Report on results

There is no mention of thermoset composite waste, EOL vehicles, or EOL aircraft management in the 5 year Action Plan. However, there are a few interesting developments. The Regulation for the Recovery and Reclamation of Products by Enterprise extends producer responsibility for several EOL products. This regulation forces companies to manage and bear the full cost of reclamation, recycling, and disposal of their waste. Another interesting development is the increase of landfilling fees discussed in the Regulation Respecting the Charges Payable for the Disposal of Residual Materials[5].

c) The Regulation on Hazardous Materials

It is important to determine whether or not thermoset composite waste is considered hazardous. The Regulation on Hazardous Materials[7] defines a hazardous material as any substance which poses a threat to health or the environment and has the following properties: explosive, gaseous, flammable, poisonous, radioactive, corrosive, oxidizing or leachable. There are also materials that are classed as hazardous regardless to whether or not they possess any of the above mentioned properties. They are:

- Oil and grease
- A contaminated empty container
- A gas cylinder or aerosol container containing a hazardous material
- A material or object containing 3 %wt. or more of oil or grease
- A material or object containing more than 1 500 mg /kg of total organic halogens
- A material containing polychloride biphenyls (PCBs) or contaminated by PCBs
- A material or object contaminated on its surface.

Hazardous materials may be disposed of in final disposal sites other than the following:

- Materials in a liquid state at 20 °C
- Materials that contain a free liquid
- Flammable or explosive materials
- Soil having 50 mg / kg of PCBs or more
- Materials physically or chemically incompatible with the materials that constitute the final disposal site
- Materials that may, on contact with water, air or materials already in the site, form gases, mists or fumes at levels that could lead to harmful effects on the health of human beings or of other living species or damage to the environment or to property
- Materials and objects containing PCBs or contaminated by PCBs.

In general, thermoset composite waste is not considered hazardous. However, the recycling of thermoset composites may produce hazardous by-products. For example, chemical and thermal recycling methods transform the resin matrix into lower chained hydrocarbons that are in a liquid or gaseous state. These by-products need to be either incinerated, combusted for energy generation purposes, or sold as a product because they cannot be sent to final disposal sites.

d) The Regulation for the Recovery and Reclamation of Products by Enterprises

This regulation promotes extended producer responsibility for electronics, batteries, paints and paint containers and mercury lamps, and will impose stringent conditions on their waste management. It states that companies must implement a recovery and re-use program for the products they market. If they fail to meet this obligation, they will have to pay to the Green Fund, an amount corresponding to the difference between the prescribed and achieved rates[8].

e) Regulation Respecting the Charges Payable for the Disposal of Residual Materials

The purpose of this regulation is to prescribe the charges payable for the disposal of residual materials in disposal sites. Every operator of a disposal site must pay charges of $10.88 / t of residual materials received for disposal. In addition, from October 1st 2010 until September 30th 2015, an additional fee of $9.50 / t is charged. However, no charge is payable for incineration residue from an incinerator or for residual materials that are sorted and recovered on the premise that they will be reclaimed[9].

### 2.1.3. Waste management in Europe

#### *2.1.3.1 Overview*

In 2008, the European Union (EU-27) produced 2.62 billion tonnes of waste amounting to 5.2 t / capita. 91% of this waste was treated, leaving 468 kg / capita that was disposed of. EU's waste management policies aim to reduce the environmental and health impacts of waste and to improve its resource efficiency. These policies are based on 3 principles; waste prevention, recycling and reuse, as well as improving final waste disposal and monitoring. The EU's 6th Environmental Action Plan includes waste prevention and management as top priorities. Its main objective is to decouple waste generation from economic activities. Therefore, with proper measures in place, economic growth should not lead to an increase in the waste volume to be disposed of[10].

EU waste directives on landfilling and incineration have resulted in stringent management conditions for composite waste. Since 2004, the landfill of composite waste has been banned by most EU member states. Member state policies have put more pressure on solving composite waste management through reuse and recycling, by promoting the waste management hierarchy and extended producer responsibility. The EU has already set recycling targets for many types of waste: EOL vehicles, electronics and electronic equipment, batteries, packaging, demolition and construction materials and municipal waste[11,12].

The Landfill Directive (1999/31/EC)[13] is intended to prevent or reduce the negative effects of waste on health and the environment. It sets strict requirements for the operation, monitoring, and closure of a landfill site. This directive defines 3 types of landfills: hazardous, non-hazardous, or inert. Co-disposal and mixing of hazardous and non-hazardous waste is not permitted. Additionally, all waste must undergo treatments to decrease its volume or to remove its hazardous nature. Therefore, composite waste is not considered an end-waste and must be processed before disposal. Certain wastes are restricted or banned from landfills such as tires, liquid waste and some types of hazardous and biodegradable wastes[10,11].

According to the United Kingdoms' waste classification scheme, composite waste is defined as a non-hazardous material under the heading of Biodegradable Wastes and other non special waste which can give rise to organic or other contamination and it can be disposed of in a

landfill that accepts non-hazardous waste[11]. The landfill directive obliges Member States to reduce the amount of biodegradable waste that they landfill to 35% of 1995 levels by 2016[14]. Therefore, some EU states have set targets to progressively reduce the amount of biodegradable waste that is sent to landfills. Moreover, under many EU state legislations, the landfilling of organic wastes, including plastics, is restricted or even banned. EU legislation does not differentiate composite waste from other types of organic wastes even though they may be relatively inert[10,11].

The directive on incineration (200/76/EC)[15] sets requirements for the emission of contaminants in the air, water, and soil. Different types of wastes are often co-incinerated so that the energy content remains relatively constant. This ensures complete combustion and avoids unwanted emissions. Composite waste can be incinerated provided that it does not exceed the limits provided by regulation. However, its high caloric content and the limited capacity of municipal incinerators means that less domestic waste, of which there's nearly an unlimited supply, is incinerated. Therefore, the cost of incinerating composite waste is much higher than ordinary waste. For example, in London, the cost of incinerating composite waste (€ 120 / t - € 150 / t) is approximately 5 times more expensive than the average (€ 30 / t)[12]. The residues produced by the incineration of composite waste would be composed of inorganic fillers and fibers and they can as such be sent to landfills[11].

Table 2 gives a list of relevant legislative documents regarding composite waste.

*Table 2. Relevant EU legislative documents regarding composite waste[11].*

| Document | Title |
|---|---|
| 75/442/EEC | The Waste Framework Directive |
| 91/689/EEC | The Hazardous Waste Directive |
| 93/259/EEC | The Regulation on Trans-border Shipment of Waste |
| 94/67/EEC | The Hazardous Waste Incineration Directive |
| 1999/31/EC | The Landfill Directive |
| 1999/45/EC | The Dangerous Preparations Directive |
| 2000/76/EC | The Incineration of Waste Directive |
| 2000/53/EC | The End-of-Life of Vehicles Directive |
| 2000/532/EC | List of Waste in relation to the Waste Framework Directive 75/442/EEC |
| 2002/95/EC | The RoHS Directive (restriction of use of hazardous substances in electrical and electronic Equipment) |
| 2002/96/EC | The Waste Electrical and Electronic Equipment Directive (WEEE Directive) |

#### *2.1.3.2. The End of Life Vehicle Directive (2000/53/EC)*

Every year, EOL vehicles generate from 8 to 9 million tonnes of waste in the EU. The EOL Vehicle Directive (2000/53/EC) aims to increase the reclamation, reuse, and recycling of EOL vehicles. It does this by imposing stringent demands on automobile manufacturers[16]:

- EOL vehicles after 2006:
  - 85 wt% must be reused, recycled, or subject to energy recovery.
  - Only 15 wt% can be landfilled.
- EOL vehicles after 2015:
  - 85 wt% must be reused or recycled.
  - 10 wt% may be subject to energy recovery
  - 5 wt% can be landfilled

The ferrous and non-ferrous metals account for approximately 76 %wt. of a vehicle and these materials are routinely reclaimed and recycled. The more difficult challenge is to reclaim and recycle plastics, which make up approximately 9 %wt. of a vehicle. Therefore, due to legislation, composite automobile suppliers may lose a portion of their market share to the metal industries if their parts cannot be reclaimed or recycled[17].

## A.2 Polyphenylene Sulfide (PPS) Composites Reinforced with Recycled Carbon Fiber

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# Polyphenylene sulfide (PPS) composites reinforced with recycled carbon fiber

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ABSTRACT

Recycled carbon fibers were reclaimed by commercial scale pyrolysis from carbon fiber reinforced thermoset composite waste generated by the aerospace industry. The mechanical and physical properties of the reclaimed carbon fibers were shown to be comparable to those of aerospace grade virgin carbon fibers. The recycled carbon fibers were integrated into a polyphenylene sulfide (PPS) thermoplastic resin by twin screw compounding followed by injection molding. Composites containing 20 wt.% and 40 wt.% recycled carbon fibers were produced. Overall, the fibers were found to be uniformly dispersed in the polymeric matrix. The tensile, flexural and impact properties of the composites were evaluated. The recycled carbon fiber reinforced PPS composites exhibited comparable mechanical properties to equivalent compounds produced using industrial grades of short virgin carbon fiber. In addition, thermogravimetric analysis showed that the introduction of recycled carbon fibers was not detrimental to the inherent thermal stability of PPS.



### 1. Introduction

Composites have been used in aircraft design for many years as they significantly reduce aircraft weight and fuel consumption. Carbon fiber reinforced polymers (CFRPs) are particularly attractive for the aerospace industry since they are light and show outstanding mechanical properties and corrosion resistance. In 2011, the worldwide demand of carbon fibers for aerospace applications was 7000 t and it was expected to increase to 19,700 t by 2020 [1]. Although CFRPs present numerous advantages, their increasing use also generates an increasing amount of waste, including out-of-date prepregs, manufacturing cut-offs, testing materials, production tools and end-of-life components [2]. In North America, there is currently nearly no legislation to curtail composite waste disposal. However, a few developments have recently been made by certain provincial governments, such as the province of Quebec (Canada) which has increased landfilling fees [3]. On the other hand, the European Union has adopted stringent management conditions with regards to composite waste, limiting their disposal by landfilling [4] and extending producer responsibility [5]. The increasing legislation on composite waste management requires the establishment of recycling routes to ensure proper conformity with upcoming regulations.

Composite recycling has been the subject of much investigation over the last decade. The recycling of thermoset composites, which account for the largest part of the aerospace composite materials, is still problematic. Several methods have been developed to recycle thermoset composites. Mechanical grinding [2,6–9], which consists of breaking down the thermoset composite waste by shredding, crushing or milling, is the most current method for recycling fiber reinforced thermoset composites. The fragments produced are typically reused as fillers in composites, artificial woods or cements. Fiber extraction, on the other hand, generates more valuable products. This is particularly true in the case of CFRPs, since the price of virgin carbon fibers lies between 32 USD/kg and 65 USD/kg, versus 18–26 USD/kg for carbon fibers reclaimed from CFRP waste [10]. In addition, the production of recycled carbon fibers requires less energy than the manufacturing of virgin carbon fibers, making former an environmentally attractive option [10].

Several technologies allow for the reclamation of carbon fibers from CFRP waste. Pyrolysis [2,6,11–13], which consists in the thermal degradation of the polymer matrix in the absence of oxygen at temperatures varying from 450 °C to 700 °C, is the most mature technology. ELG Carbon Fibre Ltd. [14] (United Kingdom) is the world's first commercial scale plant for recycling CFRPs. They have the capacity to process 2000 t/year of composite waste using

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continuous pyrolysis. Materials Innovation Technologies [15] (United States) has the capacity to process 1300 t/year to 2200 t/year of composite waste using batch pyrolysis. Catalytic conversion [2,6,16,17] aims at decomposing the polymer matrix into low molecular weight hydrocarbons using chemical solvents. It operates at temperatures comprised between 150 °C and 300 °C. Adherent Technologies Inc. [18] (United States) has developed a batch catalytic conversion process at the pilot scale. Besides pyrolysis and catalytic conversion, two other promising recycling technologies have been developed but are currently only available at the laboratory scale. The fluidised bed process [2,6,19–21] consists of a fast thermal oxidative decomposition of the polymer matrix between 450 °C and 550 °C, whereas the supercritical fluid process [2,22–25] involves the use of a solvent maintained in a supercritical state to decompose the polymer matrix. The properties of the recycled carbon fibers are tightly linked to the reclaiming process used. It has been reported that carbon fibers reclaimed by pyrolysis show little reduction in tensile strength when processed under 500 °C [6,11]. For more information, a thorough review of the existing thermoset recycling technologies has been recently published by Pimenta and Pinho [2].

As of now, recycled carbon fibers have been successfully reused as reinforcements in several thermosetting resins (e.g. epoxy [26–28]) and thermoplastic resins (e.g. polyethylene [29], polypropylene [30–32], polyamide [33], polyetherimide [33] and poly ether ether ketone [33]). McNally et al. [29] reported a 180% increase in polyethylene tensile modulus and a 27.5% increase in tensile strength using 30 wt.% milled recycled carbon fibers. Wong et al. [32] reported a 75% increase in polypropylene tensile strength using 30 wt.% short recycled carbon fibers. In this case, the addition of carefully selected maleic anhydride grafted coupling agents allowed an improvement of the adhesion at the fiber/matrix interface, resulting in further enhancements in tensile strength.

In this work, a representative sample of aerospace thermoset composite waste was collected and pyrolyzed at the commercial scale. The reclaimed carbon fibers were carefully characterized before being incorporated as reinforcements in a polyphenylene sulfide (PPS) thermoplastic matrix by twin screw extrusion. PPS is one of the most popular thermoplastics for aerospace applications due to its reasonable cost, processing temperature, high stiffness and hardness, excellent resistance to solvents and low flammability. The recycled carbon fiber reinforced PPS composites were mechanically and thermally characterized. Their properties were compared to those of equivalent composites based on virgin carbon fiber.

## 2. Materials

Ryton P-6, a low viscosity PPS grade produced by Chevron Phillips (melt flow index: 380 g/10 min at 316 °C/5 kg) was selected as the polymeric matrix to fabricate the carbon fiber reinforced thermoplastic composites.

Recycled carbon fibers were reclaimed from a 100 kg sample of carbon fiber reinforced thermoset waste provided by Bell Helicopter Textron Canada Ltd. (Mirabel, Quebec, Canada). This waste sample was representative of the actual waste composition generated by the Canadian aerospace industry. It mainly contained carbon fiber prepregs (cured and uncured) based on epoxy or bismaleimide resins, and finished parts made of carbon fiber reinforced epoxy. The finished parts also contained contaminants such as primer or paint. The pyrolysis was performed at Materials Innovation Technologies (Lake City, South Carolina, United States) using their commercial batch pyrolysis oven. Before pyrolysis, the waste was sorted and cut into 6 mm × 6 mm fragments. The waste fragments before and after pyrolysis are shown in Fig. 1. Pyrolysis was performed below 400 °C under controlled atmosphere. The duration of the process was adjusted as a function of the material to be pyrolyzed according to the expertise developed by Materials Innovation Technologies. Recycled carbon fibers were obtained from prepregs and from finished parts, both with an average length of 6 mm. The recycled carbon fibers were cleaned by successive water washings involving ultra-sonication steps to remove any pyrolysis residues, and further dried to eliminate residual moisture.

As the recycled carbon fibers originate from different feedstock, they are composed of various types of carbon fibers. Hence, it was not possible to assess precisely the effect of the reclaiming process on their properties. In this situation, the performance of the recycled fibers was compared to that of typical carbon fibers: aerospace grade, long virgin carbon fibers (Torayca® T700S; sized) were supplied by Toray, while industrial grade, short virgin carbon fibers (Panex 35; unsized; nominal length: 6 mm) were obtained from Zoltek.

## 3. Experimental

### 3.1. Characterization of the recycled carbon fibers

The surface of the recycled carbon fibers was investigated using a Jeol GSM 6100 scanning electron microscope (SEM) operating at 10 kV. The density of the recycled carbon fibers was measured using a gas picnometer Humypic from InstruQuest. The measurements were carried out at 210 kPa using a stabilization time of 300 s. Reported values are the average of three measurements. Specific area of the various types of carbon fibers was determined by nitrogen ($N_2$) BET adsorption using an Autosorb 1 MP from Quantachrome Instruments. Adsorption isotherms of nitrogen were performed at 77 K.

Micro-tensile testing was performed on mono-filaments of Torayca® T700S and recycled carbon fibers from prepregs according to standard ASTM D3379 and using an Instron Microtester equipped with a 2 N load cell. A gage length of 10 mm was used. The carbon fibers were tested at a rate of 1 mm/min. Reported values are the average of 30 samples for each type of carbon fiber.

### 3.2. Fabrication of the carbon fiber reinforced PPS composites

All materials, including the PPS resin, were dried in an oven to remove residual moisture prior to compounding. PPS and carbon fibers were compounded using a Leistritz 34 mm co-rotating twin-screw extruder comprising ten zones. PPS (in a powder state) was fed at the main hopper, while carbon fibers were fed downstream using a side feeder. The screw configuration was selected so as to minimize mechanical damage to the fibers, and contained three zones of mixing elements. The extruder was operated at a total throughput of 3 kg/h with a screw speed of 150 rpm and a die temperature of 315 °C. The extrudate was air cooled and pelletized. Specimens for mechanical testing were molded from the composites pellets using a Boy 34 t injection molding press. Injection temperature was set between 290 °C and 305 °C. Injection mold was maintained at 135 °C to allow for crystallization of PPS. Cooling time was 40 s and cycle duration was 55 s.

### 3.3. Characterization of the carbon fiber reinforced PPS composites

The tensile properties of the carbon fiber reinforced PPS composites were measured according to standard ASTM D638 using an Instron 1123 machine equipped with a 25 kN cell. Type I specimens were tested at a crosshead speed of 5 mm/min. An extensometer (50 mm, 10%) was used. Tensile modulus ($E$), maximum

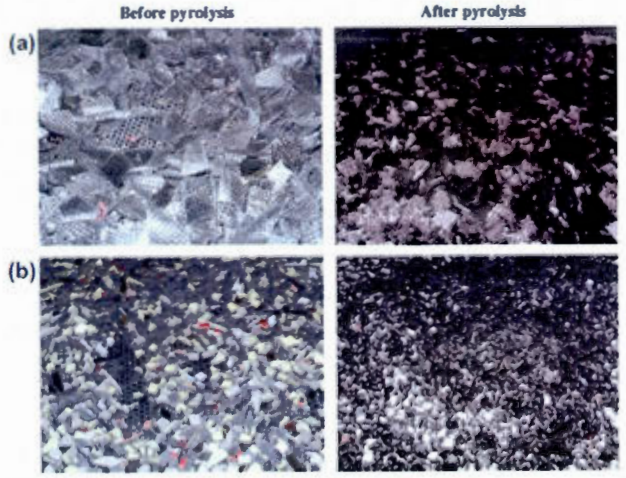


Fig. 1. General aspect of the waste composite fragments before and after pyrolysis: (a) epoxy and bismaleimide prepregs (uncured and cured); and (b) finished parts.

tensile stress ($\sigma_{max}$), elongation at break ($\varepsilon_b$) and energy to break ($E_b$) were calculated. Values reported are the average of five measurements for each composite. The fractured tensile test specimens were inspected using a field emission gun SEM Hitachi S4700 operating at 2 kV to determine the mode of failure and evaluate the adhesion at the fiber/matrix interface. Polished surfaces of untested tensile test specimens were examined using a Jeol GSM 6100 SEM operating at 10 kV to determine fiber orientation and distribution.

Flexural properties were evaluated according to standard ASTM D790 using an Instron 1123 machine equipped with a 5 kN cell. The crosshead speed was 1.3 mm/min. The span was 48 mm. Flexural modulus ($E_f$), flexural yield stress ($\sigma_{fy}$), strain at yield ($\varepsilon_{fy}$) and energy to yield ($E_{fy}$) were calculated. Values reported are the average of five measurements for each type of composite.

The impact energy ($W$) was measured using the Izod impact test (notched) according to standard ASTM D256. Specimens had a thickness of 3.17 mm and a 2 lb-ft hammer was used. Values reported are the average of 10 measurements for each composite.

The thermal properties of the carbon fiber reinforced composites were evaluated using a differential scanning calorimeter DSC Q2000 (TA Instruments) operating under nitrogen. A heating ramp from 25 °C to 350 °C at 20 °C/min was applied. The melting temperature ($T_m$) and the initial crystal content ($\chi_0$) were evaluated. The crystal content was calculated according to:

$$\chi_0 = \frac{\Delta H_m}{f * \Delta H_m^0} \quad (1)$$

where $\Delta H_m$ is the enthalpy of fusion, $\Delta H_m^0$ is the enthalpy of fusion of 100% crystalline PPS and $f$ is the effective PPS weight fraction in the composite. In this work, we employed the value of $\Delta H_m^0$ reported by Huo and Cebe [34] (112 J/g).

Finally, the thermal stability of the carbon reinforced PPS composites was evaluated using a thermogravimetric analyzer TGA/DSC1 (Mettler Toledo). A heating ramp was applied from 25 °C to 700 °C at 20 °C/min under nitrogen and air atmospheres. We report temperatures at 5 wt.% and 10 wt.% degradation ($T_{d5}$ and $T_{d10}$), as well as the mass of the residue at 700 °C.

## 4. Results and discussion

### 4.1. Characterization of recycled carbon fibers

The length distribution of recycled carbon fibers was characterized on a population of 619 individual recycled fibers from

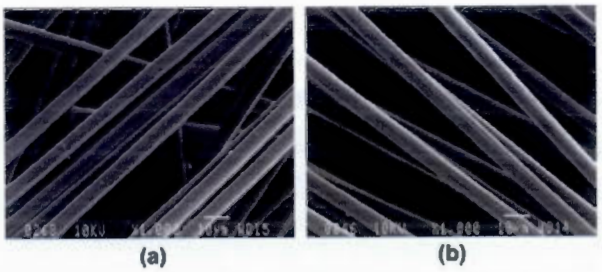


Fig. 2. Aspect of recycled carbon fibers after cleaning: (a) recycled carbon fibers from prepregs; and (b) recycled carbon fibers from finished parts.

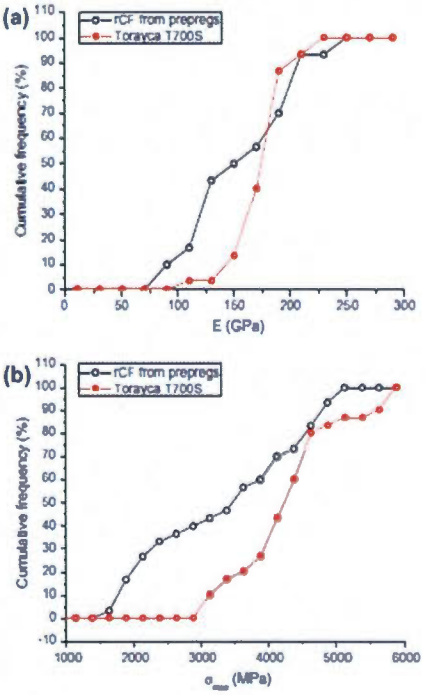


Fig. 3. Cumulative frequency distributions of (a) tensile modulus ($E$) and (b) tensile stress at maximum load ($\sigma_{max}$) for recycled carbon fibers from prepregs (average: $\langle E\rangle$ = 165 GPa; $\langle\sigma_{max}\rangle$ = 3425 MPa) and virgin carbon fibers Toraycа® T700S (average: $\langle E\rangle$ = 182 GPa; $\langle\sigma_{max}\rangle$ = 4385 MPa).

prepregs using image analysis. The average length was 5.6 mm (standard deviation: 1.5 mm; 95% confidence interval: 5.5–5.8 mm). Although not characterized, recycled carbon fibers from finished parts are expected to have a similar length distribution as they were obtained using the same process. The physical appearance of recycled carbon fibers from prepregs and from finished parts was examined by SEM. The recycled fibers were clean and exhibited an average diameter of 6.5 μm (Fig. 2). The average density of the recycled carbon fibers from prepregs was 1.75 g/cm$^3$. This value is close to theoretical density of virgin carbon fibers (1.8 g/cm$^3$), which further confirms the good quality of the reclaimed fibers. Specific area of the fibers was determined by $N_2$ BET adsorption. Panex 35 unsized virgin carbon fibers were shown to have a specific area of 1 m$^2$/g and to contain nearly no pores. Recycled carbon fibers from prepregs and from finished parts exhibited much higher specific areas (respectively 4.2 m$^2$/g and 1.8 m$^2$/g), which might indicate a deterioration of the surface of the carbon fibers during the pyrolysis process.

The tensile properties of the recycled carbon fibers from prepregs were evaluated using micro-tensile testing. Recycled carbon fibers are reclaimed from a diverse feedstock based on various types of carbon fibers. Hence, they are actually composed of a mixture of different populations. For sake of simplicity, we selected a single aerospace grade reference material (Toraycа® T700S) for comparison purposes. The cumulative frequency distributions of tensile modulus and tensile strength of Toraycа® T700S and recycled carbon fibers from prepregs are plotted in Fig. 3. As expected, recycled carbon fibers from prepregs show a broader distribution in tensile modulus and tensile strength than Toraycа® T700S fibers. However, they retain overall good properties after pyrolysis, with an average tensile modulus of 165 GPa and an average tensile strength of 3425 MPa. Compared with Toraycа® T700S fibers, this represents a difference of −10% in average tensile modulus and −22% in average tensile strength.

### 4.2. Characterization of carbon fiber reinforced PPS composites

The properties of the carbon fiber reinforced PPS composites were evaluated in tension. As expected, composites containing carbon fibers showed enhanced tensile properties compared to pure PPS (Table 1). For a 40 wt.% recycled carbon fiber content, the tensile modulus was increased by 680%, the maximum tensile stress by 680–720%, the elongation at break by 20–35%, and the energy to break (which is an indication of the toughness) by 910–1100%. The tensile properties of the PPS composites made from recycled carbon fibers were slightly higher than those made from Panex 35 short carbon fibers. According to the technical data of the supplier, Panex 35 short carbon fibers have a tensile modulus of 242 MPa and a tensile strength of 4137 MPa. Although it was not possible to verify those values by micro-tensile testing because of the short length of Panex 35 fibers (6 mm), it is unlikely that

**Table 1**
Tensile properties of PPS and carbon fiber reinforced PPS composites (error on measurements corresponds to the standard deviation; $A$ is the variation expressed in % with respect to the pure PPS matrix). Theoretical tensile moduli are also given for a PPS composite reinforced with recycled carbon from prepregs as a function of fiber content and fiber orientation.

| | Reinforcement (wt.%) | $E$ (GPa) | $A$ (%) | $\sigma_{max}$ (MPa) | $A$ (%) | $\varepsilon_b$ (%) | $A$ (%) | $E_b$ (J) | $A$ (%) |
|---|---|---|---|---|---|---|---|---|---|
| PPS | – | 3.9 ± 0.2 | – | 24 ± 6 | – | 0.66 ± 0.18 | – | 0.17 ± 0.08 | – |
| PPS/vCF Panex 35 | 20 | 14.7 ± 0.5 | 277 | 107 ± 3 | 343 | 0.84 ± 0.03 | 27 | 0.94 ± 0.05 | 453 |
| PPS/rCF from prepregs | 20 | 16.8 ± 0.2 | 332 | 133 ± 5 | 447 | 0.86 ± 0.04 | 30 | 1.19 ± 0.12 | 600 |
| PPS/rCF from finished parts | 20 | 17.4 ± 0.5 | 346 | 146 ± 4 | 499 | 0.97 ± 0.06 | 47 | 1.52 ± 0.18 | 794 |
| PPS/vCF Panex 35 | 40 | 30.5 ± 3.1 | 684 | 174 ± 2 | 618 | 0.88 ± 0.08 | 33 | 1.85 ± 0.22 | 988 |
| PPS/rCF from prepregs | 40 | 30.3 ± 1.6 | 680 | 200 ± 5 | 723 | 0.89 ± 0.06 | 35 | 2.04 ± 0.15 | 1100 |
| PPS/rCF from finished parts | 40 | 30.3 ± 0.3 | 680 | 191 ± 3 | 687 | 0.80 ± 0.02 | 21 | 1.72 ± 0.12 | 912 |
| *Theoretical values* | | | | | | | | | |
| PPS/rCF from prepregs | 20 | 8.6 ($\chi_1$ = 1/5)<br>13.3 ($\chi_1$ = 3/8)<br>30.1 ($\chi_1$ = 1) | | | | | | | |
| PPS/rCF from prepregs | 40 | 13.8 ($\chi_1$ = 1/5)<br>23.7 ($\chi_1$ = 3/8)<br>58.9 ($\chi_1$ = 1) | | | | | | | |

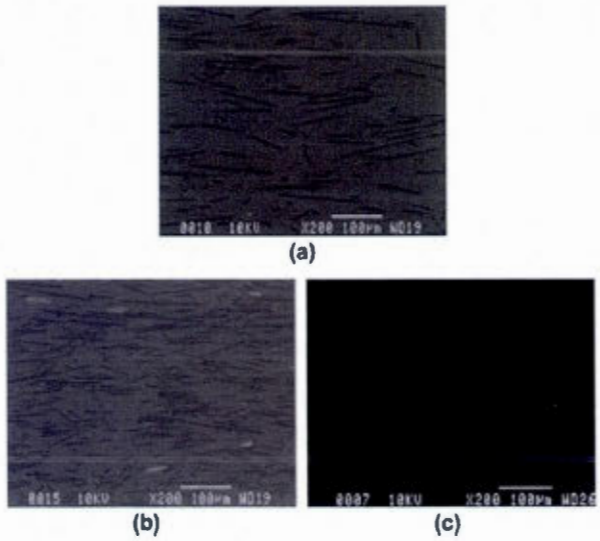


Fig. 4. SEM observation of polished specimens of PPS composites: (a) 20 wt.% recycled carbon fibers from prepregs; (b) 40 wt.% recycled carbon fibers from prepregs (white particles are glass fibers present in the composite waste); and (c) 40 wt.% Panex 35.

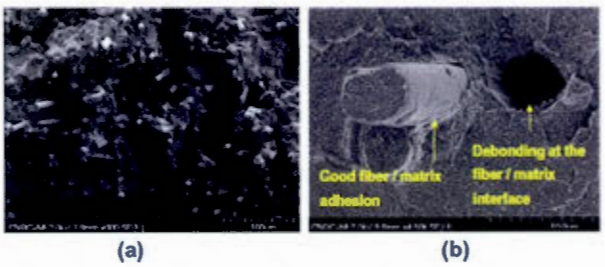


Fig. 5. Fractured surfaces of PPS composites reinforced with recycled carbon fibers from prepregs (40 wt.%): (a) overview at low magnification; (b) details at high magnification.

recycled carbon fibers have better intrinsic tensile properties than Panex 35. Other possible explanations for the better performance of the PPS composites made from recycled carbon fibers might be: (i) differences in dispersion and/or distribution of the carbon fibers in the matrix, and (ii) differences in adhesion at the PPS/carbon fiber interface.

As a first approximation, the longitudinal tensile modulus of short fiber composites can be evaluated using the following rule of mixture, based on the shear-lag theory developed by Cox [35] for short fibers perfectly bonded to the matrix, and modified by Hull to take into account the orientation of the fibers [36]:

$$E_c = \chi_1 \chi_2 v_f E_f + v_m E_m \quad (2)$$

In this equation, $E_f$ and $E_m$ are the respective tensile moduli of the fiber and the matrix, $v_f$ and $v_m$ are the respective volume fractions of the fiber and the matrix, $\chi_2$ is a parameter comprised between 0 and 1 depending on the aspect ratio of the fibers and the distance between fibers, and $\chi_1$ is a parameter comprised between 0 and 1 accounting for the orientation of the fibers ($\chi_1 = 1$ for fibers parallel to the stress direction, $\chi_1 = 3/8$ for in plane randomly distributed fibers, $\chi_1 = 1/5$ for three-dimensionally randomly distributed fibers and $\chi_1 = 0$ for fibers perpendicular to the stress direction). In this study, the following parameters were used: $E_f = 165$ GPa (Fig. 3), $E_m = 3.9$ GPa (Table 1) and $\chi_2 \approx 1$ due to the high aspect ratio of the fibers (length: 6 mm; diameter: 6.5 μm; possible attrition of the fibers during the extrusion process is not considered here). Table 1 also gives the theoretical tensile modulus of a PPS composite reinforced with recycled carbon fibers from prepregs as a function of the fiber content and of the fiber orientation parameter $\chi_1$. The results suggest that the recycled carbon fibers are probably in-plane distributed and randomly oriented. To validate this result, SEM observations were performed on polished

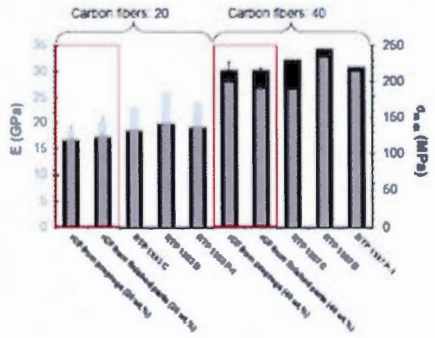


Fig. 6. Tensile properties of PPS composites reinforced with recycled carbon fibers and commercial PPS compounds reinforced with short virgin carbon fibers [37]. Error bars refer to the standard deviation.

longitudinal sections of the injected specimens. The micrographs confirm that the recycled carbon fibers are essentially aligned along the injection direction and are evenly distributed in the matrix (Fig. 4). The dispersion and distribution are very similar for PPS composites reinforced with Panex 35 short carbon fibers.

The fractured surfaces of the tensile test specimens were observed by SEM. Good adhesion was generally observed at the fiber/matrix interface despite the absence of any sizing on the surface of the fibers (Fig. 5). Although the occurrence of debonding at fiber/matrix interface can be observed, failure by fiber rupture seems to be the predominant mechanism. This result is consistent with the increase in elongation at break observed for the carbon fiber reinforced composites, since carbon fibers have a higher elongation at break than pure PPS.

Finally, the tensile properties of the PPS composites reinforced with recycled carbon fibers were compared to those of commercial PPS compounds from RTP Company containing 20 wt.% and 40 wt.% virgin carbon fibers [37]. The results, summarized in Fig. 6, clearly demonstrate that short recycled carbon fibers have the potential to compete with their virgin equivalents.

Flexural properties are reported in Table 2. For a 40 wt.% recycled carbon fiber content, the flexural modulus was increased by 530% and the flexural stress at yield by 290–310% compared to pure PPS. Despite a decrease of 30% in the strain at yield, the energy to yield is increased by 170–210% compared to pure PPS. Consistent with the tensile testing results, the flexural properties of the PPS composites made from recycled carbon fibers exhibited were found to be higher than those made from Panex 35 short carbon fibers. In addition, the products made from recycled carbon fibers exhibit similar flexural properties to commercial compounds from the RTP Company based on virgin carbon fibers [37].

**Table 3**
Impact properties of PPS and carbon fiber reinforced PPS composites (error on measurements corresponds to the standard deviation; $A$ is the variation expressed in % with respect to the pure PPS matrix).

| | Reinforcement (wt.%) | $W$ (J/m) | $A$ (%) |
|---|---|---|---|
| PPS | – | 13 ± 0 | – |
| | | | 123 |
| PPS/vCF Panex 35 | 20 | 29 ± 1 | 123 |
| PPS/rCF from prepregs | 20 | 37 ± 2 | 192 |
| PPS/rCF from finished parts | 20 | 38 ± 3 | 185 |
| | | | 254 |
| PPS/vCF Panex 35 | 40 | 39 ± 2 | 200 |
| PPS/rCF from prepregs | 40 | 46 ± 6 | 246 |
| PPS/rCF from finished parts | 40 | 45 ± 2 | 254 |

Izod impact resistance of the composites is reported in Table 3. The PPS composites containing recycled carbon fibers show enhanced properties compared to pure PPS and to composites made from Panex 35 short carbon fibers. For a 40 wt.% recycled carbon fiber content, the impact energy was increased by 250% compared to pure PPS.

The crystal content of injected samples of neat PPS and PPS composites reinforced with recycled carbon fibers from prepregs was evaluated by DSC. The results, summarized in Table 4, show that injection molding produces specimens having a degree of crystallinity of about 38 wt.%, regardless of the carbon fiber content. Therefore, the increase in mechanical properties should be mainly attributed to the presence of carbon fibers and is not associated to a change in material crystallinity. The thermal stability was evaluated by TGA. Results are reported in Table 4. The incorporation of recycled carbon fibers is not detrimental to the inherent thermal stability of PPS and the onset of degradation ($T_{d5}$) remains approximately 515 °C for all samples. Furthermore, the presence of recycled carbon fibers leads to an increase of the carbonaceous residue at 700 °C, which reaches 60–70 wt.%. This result is of industrial interest since charring of polymers during their combustion improves fire retardancy.

## 5. Conclusions

In this work, carbon fibers were reclaimed by commercial scale pyrolysis from carbon fiber reinforced thermoset composite waste generated by the aerospace industry. Micro-tensile testing and density measurements showed that the reclaimed carbon fibers retained satisfactory properties. The recycled carbon fibers were compounded with PPS to obtain composites containing 20 wt.% and 40 wt.% recycled carbon fibers. The tensile, flexural and impact properties of the composites were evaluated. It was demonstrated that PPS composites reinforced with recycled carbon fibers exhibit similar or better mechanical properties than equivalent commercial compounds produced using industrial grade short virgin carbon fibers. This confirms the huge potential of carbon fibers reclaimed from CFRP waste to be incorporated as reinforcements

**Table 2**
Flexural properties of PPS and carbon fiber reinforced PPS composites (error on measurements corresponds to the standard deviation; $A$ is the variation expressed in % with respect to the pure PPS matrix).

| | Reinforcement (wt.%) | $E_f$ (GPa) | $A$ (%) | $\sigma_{fy}$ (MPa) | $A$ (%) | $\varepsilon_{fy}$ (%) | $A$ (%) | $E_{fy}$ (J) | $A$ (%) |
|---|---|---|---|---|---|---|---|---|---|
| PPS | – | 4.5 ± 0.2 | – | 79 ± 13 | – | 1.74 ± 0.24 | – | 0.15 ± 0.04 | – |
| PPS/vCF Panex 35 | 20 | 12.6 ± 0.1 | 179 | 166 ± 4 | 110 | 1.35 ± 0.03 | −22 | 0.24 ± 0.01 | 60 |
| PPS/rCF from prepregs | 20 | 16.3 ± 0.4 | 259 | 220 ± 7 | 178 | 1.43 ± 0.05 | −18 | 0.34 ± 0.02 | 127 |
| PPS/rCF from finished parts | 20 | 16.9 ± 0.5 | 274 | 233 ± 5 | 195 | 1.45 ± 0.02 | −17 | 0.37 ± 0.01 | 147 |
| PPS/vCF Panex 35 | 40 | 24.3 ± 0.5 | 438 | 260 ± 5 | 229 | 1.17 ± 0.02 | −33 | 0.34 ± 0.01 | 127 |
| PPS/rCF from prepregs | 40 | 28.6 ± 1.0 | 533 | 310 ± 7 | 292 | 1.19 ± 0.04 | −32 | 0.41 ± 0.02 | 173 |
| PPS/rCF from finished parts | 40 | 28.7 ± 0.4 | 534 | 325 ± 4 | 311 | 1.28 ± 0.04 | −26 | 0.47 ± 0.02 | 213 |

**Table 4**
Thermal properties of PPS and PPS composites reinforced with recycled carbon fibers from prepregs (as determined by DSC and TGA).

| | Reinforcement (wt.%) | $\chi_c$[a] (%) | $T_m$[b] (°C) | Air, 20 °C/min | | | $N_2$, 20 °C/min | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $T_{d5}$[b] (°C) | $T_{d50}$[b] (°C) | Residue[c] (wt.%) | $T_{d5}$[b] (°C) | $T_{d50}$[b] (°C) | Residue[c] (wt.%) |
| PPS | – | 38 | 280 | 512 | 524 | 22 | 513 | 519 | 49 |
| PPS/rCF from prepregs | 20 | 38 | 279 | 516 | 530 | 58 | 514 | 527 | 61 |
| PPS/rCF from prepregs | 40 | 38 | 279 | 519 | 534 | 58 | 513 | 529 | 69 |

[a] Error on crystal content is ±1%.
[b] Error on temperature is ±1 °C.
[c] Residue is evaluated at 700 °C. Error on residue is ±2%.

in new composites. Such materials might be used for suitable applications either in the aerospace industry or in other markets.

## Acknowledgements

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